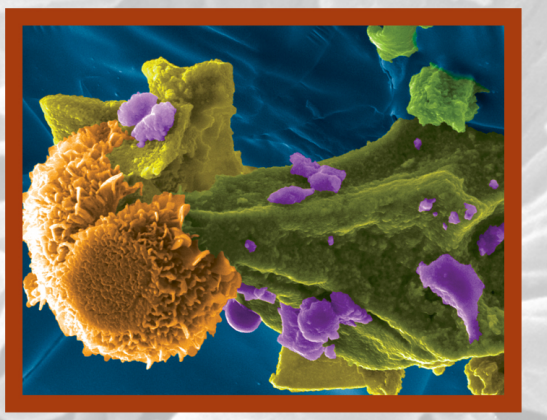
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

at Pacific Northwest National Laboratory

ANNUAL REPORT 11



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PNNL-21238

Laboratory Directed Research and Development Annual Report

Fiscal Year 2011

March 2012

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Pacific Northwest National Laboratory
Richland, Washington 99352

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Acknowledgments

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

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Laboratory Director's Message

Every day, scientists and engineers at Pacific Northwest National Laboratory make important discoveries and deliver critical technical solutions to the most intractable challenges that face our nation. As a multi-disciplinary, multi-program national laboratory, a hallmark of PNNL is our ability to advance the frontiers of science and deliver solutions in energy, environment, and security.

Our Laboratory's discretionary investments in Laboratory Directed Research and Development are essential to advancing PNNL's Laboratory Strategy and delivering our mission outcomes. LDRD investments help us nurture science and technology capabilities while capitalizing on the breadth of our staff talents. This document describes how we carefully conduct our LDRD program in compliance with the objectives and guidelines as outlined by DOE. We use rigorous internal and external peer review to maintain the scientific value and soundness of the research programs it enables.

With great pride in our researchers' accomplishments, I present PNNL's Fiscal Year 2011 Laboratory Directed Research and Development Annual Report.

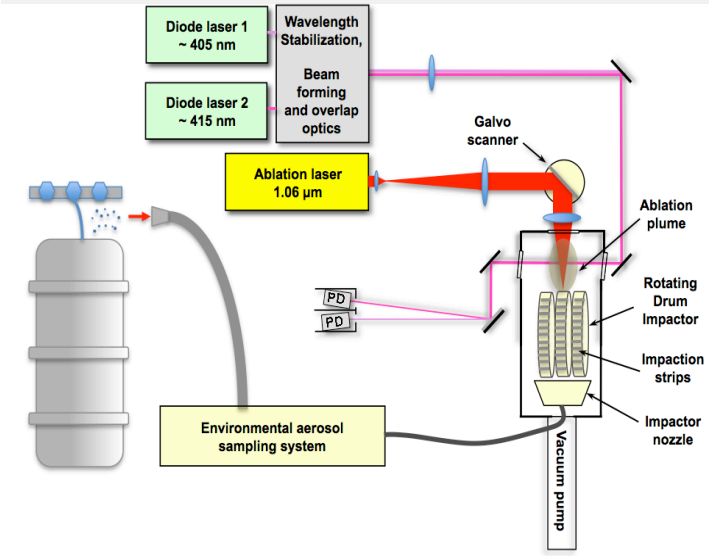
Advanced Sensors and Instrumentation

Advanced Environmental Sampling Technology for Safeguards and Proliferation Detection

Norman C. Anheier, Shane M. Peper, David C. Gerlach, M. Lizabeth Alexander

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

Environmental sampling is a critical verification tool for the implementation of safeguards and for detecting proliferation activities. Under formal agreements, safeguards inspectors are granted access to nuclear sites to collect samples. Proliferation detection and verification of peaceful nuclear activities are critical national security mission activities, underpinned by sophisticated technology that requires continuous capability improvements as the existing threats grow and new threats emerge. The expected outcomes of this research are to develop and evaluate new environmental sample collection technologies to improve collection efficiency, significantly reduce the time and cost associated with subsequent laboratory analysis, and to demonstrate that PNNL-developed laser ablation, absorbance ratio spectrometry (LAARS) can be used in a purpose built configuration to perform unattended near real-time monitoring of large enrichment facilities.



An integrated environmental aerosol collection system and LAARS instrument for continuous, on-site uranium enrichment analysis.

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

Continuing from FY 2009, progress in FY 2010 included evaluating additional new materials for increasing collection efficiencies of key analytes of interest relevant to safeguards and proliferation detection. A polymer synthesis laboratory capability was set up, and several batches of a new methacrylic copolymer were synthesized and evaluated for their ability to adhere particulates. Additionally, several commercially available conductive polymers were evaluated using SIMS to determine which one(s) would be ideal for direct sample analysis (based on degree of conductivity and strength of the analytical signal, processed by the SIMS instrument). It was determined that polyethylenedioxothiophene-poly(styrene) sulfonate (PEDOT-PSS) performed optimally.

During FY 2011, a fluorescence microspectroscopy system was developed and used to determine various chemical species associated with the nuclear fuel cycle. Single grain analysis of alpha-UO_3 was performed using this fluorescence system. Even though it was characterized as “pure” using bulk analysis techniques, our system was able to distinguish between unreacted uranyl peroxide (metastudtite) used to fabricate the oxide and the first hydrolysis product of the alpha-UO_3 allowing us potentially to monitor the kinetics of particle aging in various systems of nonproliferation interest.

These results were presented at this year's IUPAC World Chemistry Congress. Together with single crystal XRD and the micro-Raman spectroscopy system, we are poised to provide a wide array of complementary structural information regarding the chemical forms of target compounds (prior to isotopic analysis).

We evaluated the feasibility to adapt the PNNL-developed LAARS into a uranium enrichment facility safeguards technology. Our initial isotope analysis began on certified volumetric-releasable uranium standards. Research planned for FY 2012 requires uranium samples that exceed the volumetric-release threshold and therefore required work to be conducted under a radiation work permit (RWP) within a fume hood. A new laser isotope analysis laboratory was developed to support the research and a room remodeled to provide the infrastructure needed to support the class IV laser operation. Additionally, the experimental configuration was re-designed to allow uranium isotope analysis within the confines of the laboratory fume hood. A 2 ft × 2 ft optical breadboard was cantilevered from the optical table to support the LAARS ablation sample chamber within the hood. Optical alignment and operational experience was achieved using gadolinium. Initial uranium sample measurements began at the end of FY 2011, with planned mixed particulate uranium sample analysis for FY 2012. Technical progress included four major papers, and a presentation at the annual INMM meeting.

In FY 2012, we will develop methods to improve and modify an aerosol sample collector to accommodate SIMS planchets coated with thin films of conductive polymers. Anthropogenic and naturally occurring particulate uranium samples will be characterized using Raman and fluorescence microspectroscopies in order to elucidate chemical enrichment signatures. Spectral libraries of various anthropogenic and naturally occurring uranium-bearing materials will be developed to facilitate rapid particle classification and rationale selection of particles of interest. LAARS measurements will begin on uranium aerosols. Prepared enriched uranium aerosol samples (both homogeneous and trace heterogeneous) will be analyzed by LAARS to determine the uranium assay performance.

Development of an Autonomous and Configurable Marine Platform for Continuous and Long-term Monitoring of Near Shore Coastal Waters

Gary A. Gill, Jennifer L. Elster, Mark E. Jones, Michael Hughes, James R. Skorpik

◆ We will demonstrate the feasibility and suitability of integrating specific biogeochemical (e.g., pH and oxygen) and hydrographic (e.g., salinity and temperature) sensors on a commercially available unmanned marine platform. This system will fill a critical niche in a broader earth observation system network currently under development to study climate change impacts. ◆

Currently, there is lack of understanding regarding how the coastal ocean and its critical ecological resources will respond to climate change. Understanding how climate change impacts such as ocean acidification and hypoxia manifest in and effect the coastal ocean is possible only through long-term, in-situ, and continuous time-series measurements from multiple monitoring stations.

This project seeks to develop and demonstrate the usefulness of a new, low cost sampling approach using an unmanned, self-propelled, autonomous maritime vehicle (a sampling platform) capable of collecting continuous and long-term biogeochemical (oxygen, pH, nutrients, carbon dioxide, etc.) and hydrodynamic information (salinity, temperature) in the near shore coastal marine environment. The major work effort for this project is to integrate physically and electronically commercially available biogeochemical sensors into a maritime vehicle called the Wave Glider™.

Wave Glider. The Wave Glider is an unmanned, autonomous maritime vehicle manufactured by Liquid Robotics, Inc. that can operate for months to a year collecting fine temporal and spatial scale information. It is self-propelled, using ocean waves for propulsion. The system has the ability to traverse large areas of the ocean (point-to-point), maintain a fixed position and respond to preset or operational commands from shore-based facilities. The Wave Glider is a configurable platform designed to support a wide variety of sensor payloads (80 lbs) powered by solar panels/Li-ion batteries to provide power to integrated payloads. Data can be stored internally and transmitted to shore via satellite through an on-board RF transmitter or Xbee communicator. Command, control, and telemetry signals can be transmitted in real time via satellite.

Biogeochemical Sensors. The sensors chosen for this effort are an oxygen optode from Aanderaa Data Instruments, a pH electrode from InSitu, Inc., and an optical absorption sensor from WET Labs (ECO triplet) that can monitor three independent wavelengths.

The water quality sensors were physically and electronically integrated into the Wave Glider. Electronic integration was accomplished through development of a single board computer (ARM9-Atmel AT91SAM9G20, EMAC, Inc.) and RF transmitter (range >1000 feet) that remotely turned the sensors on and off. The single board computer was developed to integrate with up to 6 serial/4 analog/2 USB inputs allowing the flexibility of integrating various sensors into the platform. The RF link is also used to transmit data and health status information. The sensors were powered through internal batteries that are trickle charged through the top-mounted solar cells. In this configuration, the sensor platform could operate for extended deployment periods, collecting and logging data unattended.

September 2011 deployment of the Wave Glider integrated with water quality sensors (oxygen, pH, and optical absorption) collecting data along a predefined course in Sequim Bay.

With the three integrated water quality sensors, the Wave Glider™ was deployed for initial testing from PNNL's Marine Science Laboratory research vessel on Sequim Bay in September 2011. The sensors were mounted to the skeg portion of the surface float for this deployment, but there is flexibility in the design to put the sensor lower in the water column. The Wave Glider was programmed to follow a predetermined track within Sequim Bay and collected spatial and temporal data from collocated sensors. The onboard single board computer simultaneously collected data from the sensors. Data were stored on board the Wave Glider in a removable secure digital memory card and was also transmitted through the integrated RF transmitter to a USB/netbook PC receiver on the deployment vessel to test remote data collection capability (at 8 data bytes for each sensor). Although the deployment test period was less than a day in duration, all three sensors showed evidence of constituent changes, suggesting that they were sensitive enough for environmental monitoring for climate change research.

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

John E. Shilling, Chen Song, Naruki Hiranuma

◆ As noted by the Intergovernmental Panel on Climate Change, the effect of airborne particles (aerosols) on climate remains a great source of uncertainty for climate models. Laboratory experiments investigating the life-cycle of organic atmospheric particles, which are a large fraction of all atmospheric particles, is the focus of this project. ◆

Measurements show that organic aerosol particles comprise 20 to 90% of the total atmospheric aerosol mass. A significant portion of this organic mass (63 to 95%) is secondary organic aerosol (SOA), which forms in the atmosphere from oxidation of gas-phase hydrocarbons. However, models have difficulty in reproducing the SOA levels observed in the atmosphere. Accurate reproduction of aerosol concentrations has important consequences for reducing the uncertainties associated with the effect of aerosol on global climate change. Therefore, insights into SOA formation and transformations, radiative properties, and the ability of SOA particles to form liquid water and ice clouds will directly improve predictions of global climate change.

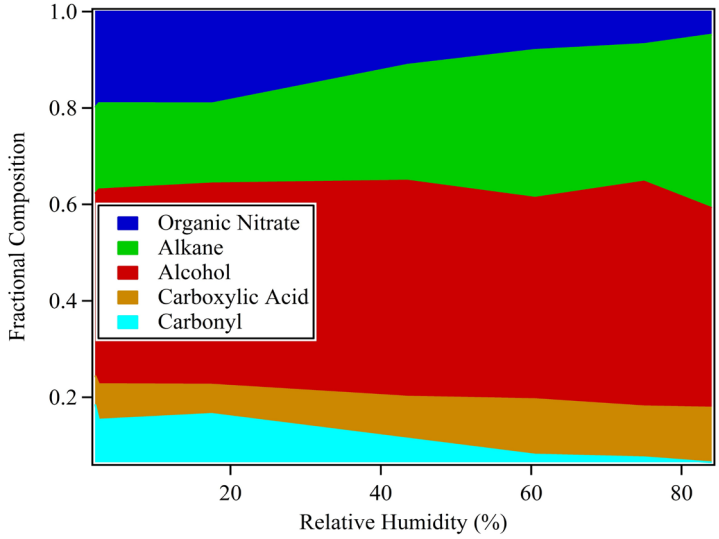
Due to limitations with the traditional experimental design, most laboratory SOA studies were conducted using high concentrations of reactants that are not representative of the real atmosphere. It is becoming clear that data collected under these conditions cannot be accurately extrapolated to atmospheric conditions and are therefore of limited use to modelers. To overcome these limitations, the lead author helped to develop continuous-flow environmental chambers, which allow experiments to be conducted under atmospheric conditions. This new capability at PNNL is now in place and is being used to conduct laboratory-based research targeted at reducing the uncertainty associated with representing the SOA formation and processing in models. Data collected in these studies will be incorporated into climate models developed by PNNL to determine the effect of aerosol particles on climate change. The chamber represents a new and unique capability for PNNL.

In FY 2009, two papers describing the chemical composition and cloud condensation nucleus activity of SOA particles were completed and published. Instrumentation was procured for the new chamber and a smaller, more limited flow-through chamber was constructed so that scientific progress could be made concurrent with development of the state-of-the-art chamber facility. By the end of that fiscal year, experiments were conducted to measure the SOA yield from the dark ozonlysis of α-pinene under atmospherically relevant conditions. The results agreed well with literature data obtained under similar conditions, validating the chamber design and performance.

The FY 2009 α-pinene ozonolysis experiments served as a baseline for experiments investigating the mixing of multiple SOA precursors conducted in FY 2010. In these experiments, we measured the ozonolysis SOA yield from pure cyclohexene, a model anthropogenic volatile organic compounds and from mixtures of cyclohexene and α-pinene. Using yield data obtained for the pure compounds, we can predict the results of the mixture experiments, assuming two conditions: α-pinene and cyclohexene SOA are fully miscible and α-pinene and cyclohexene form separate phases. Comparisons of the predicted results with the experimental data show that SOA from these species are fully and mutually soluble in each other. Thus, the particle mass produced from co-condensation of these SOA species is significantly greater than the sum of yield expected to be produced from the individual species.

In FY 2011, we collaborated to develop a new technique for differentiating atmospheric particles that form cloud droplets from those that do not. To accomplish this, an aerosol sample was passed through a cloud condensation nucleus chamber to activate some particles into droplets. Activated droplets were separated from non-activated droplets using a counterflow virtual impactor previously developed. The water was then evaporated, and the residual material was chemically analyzed with two particle mass spectrometers. A two-component external mixture of monodisperse particles was exposed to a supersaturation which would activate one of the types (ammonium sulfate) but not the other (polystyrene latex spheres). The mass spectrum observed after separation indicated only the former, validating separation of droplets from unactivated particles. Results from ambient measurements indicated that aerosol particles often activate predominantly as a function of particle size. Chemical composition is not irrelevant, however, and we observed enhancement of sulfate in droplet residuals using single particle analysis.

Also in FY 2011, the new, dual-sided, continuous-flow chamber was completed in new space in the Atmospheric Measurements Laboratory. We are currently investigating the effect of water vapor on the yield, cloud condensation nuclei (CCN) activity, and chemical composition of aerosol particles generated from α-pinene ozonolysis. Our preliminary results show that water vapor had a larger effect on aerosol properties when small atmospherically relevant amounts of α-pinene were oxidized than when larger amounts of α-pinene were oxidized. Particle yield increased by 20% at the lowest, most atmospherically relevant α-pinene-concentrations. No change was observed at higher α-pinene concentrations. The CCN activity of the particles is anti-correlated with relative humidity; higher relative humidity resulted in less CCN active particles. The atmospheric implication is that chemical composition and CCN activity of aerosol particles changes with relative humidity.



Chemical composition of SOA particles generated from the photooxidation of trimethyl benzene as a function of relative humidity. The data show organic nitrate species are hydrolyzed to alcohols as relative humidity increases, likely in the particle phase. Carbonyl groups may also be replaced by carboxylic acid, likely as a result of differences in gas-phase chemistry.

In collaboration with the University of California, San Diego, we conducted chamber experiments, investigating organonitrate hydrolysis. In these experiments, organic aerosol was produced from the photoxidation of trimethyl benzene at variable relative humidity. We found that organic nitrates are formed with a particle phase yield of ~20%, but hydrolyze to form alcohols as relative humidity increases. Concurrent with the hydrolysis of the organic nitrate functional groups, we observed a marked decrease in the absorption of blue visible light by the particles. These experiments show that: 1) organic nitrates may be an important component of freshly produced particles, 2) particulate organic nitrates would be converted to alcohols on timescales of several hours under typical atmospheric conditions, and 3) the radiative properties of aerosol particles may be affected by the chemical composition of the particles.

In Situ High-Pressure X-Ray Diffraction Investigation of Caprock Mineral Reactions With Water Solvated in Supercritical CO_2

H. Todd Schaef, Kevin M. Rosso

◆ The objective of this project is to develop a high-pressure x-ray diffraction capability to advance our understanding of reaction processes and kinetics at the fluid-solid interface between water-solvated in supercritical carbon dioxide ($scCO_2$) and minerals with special emphasis on layer silicates. ◆

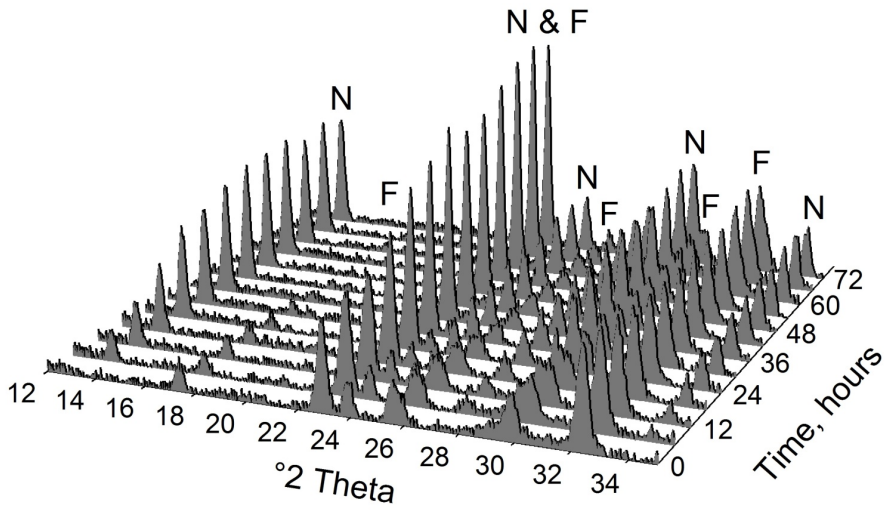
Deep saline reservoirs with confining layers (cap rocks) are considered primary targets for carbon storage by most countries. Post-injected CO_2 will reside largely as a water rich supercritical buoyant fluid, constrained from vertical migration by a very low-permeability cap rock seal. This process allows time for slow trapping mechanisms (e.g., CO_2 dissolution in pore water, precipitation of carbonate minerals) to sequester CO_2 from the system. Despite this very well-accepted conceptual model, most of the research on flow, transport, and chemical reaction processes has remained in aqueous-dominated geologic systems, which will not represent the vast majority of the rock volume where $scCO_2$ is stored. Moreover, recent work at PNNL indicates that chemical reaction processes between the water solvated in $scCO_2$ phase and geologic media are significant.

This project is developing and conducting proof-of-concept testing using high-pressure micro-focused x-ray diffraction (HXRD) capabilities to investigate fundamental reaction processes occurring in mineral systems exposed to water solvated in $scCO_2$. The in situ probe utilizes x-rays to examine transformation reactions of minerals and their kinetics when exposed to water bearing $scCO_2$ fluids under pressure, temperature, and fluid composition conditions relevant to geologic sequestration of CO_2.

Designing a reactor compatible with x-rays and acid gas mixtures requires special materials and unique design criteria. Additionally, the design must account for beam configuration, geometries at low angles, and x-ray attenuation by dense gas mixtures. During the first year of funding, a high pressure reactor was designed, fabricated, and tested at pressures and temperatures relevant to geologic sequestration. In the project's second year, testing was conducted on pure minerals, including brucite, montmorillonite, and forsterite.

In FY 2011, we used in situ HXRD to examine the carbonation of brucite [$Mg(OH)_2$] in wet $scCO_2$ at pressure (82 bar) as a function of water concentration and temperature (50°C and 75°C). Exposing brucite to anhydrous $scCO_2$ at either temperature resulted in little or no detectable reaction over three days. However, addition of trace amounts of water resulted in partial carbonation of brucite into nesquehonite [$MgCO_3 \cdot {}_3H_2O$] within a few hours at 50°C. By increasing water content to well above the saturation level of the $scCO_2$, complete conversion of brucite into nesquehonite was observed. Tests conducted at 75°C resulted in the conversion of brucite into magnesite [$MgCO_3$] instead, apparently through an intermediate nesquehonite step.

Testing with an expandable clay (montmorillonite), which is common to caprock formations, under three basic scenarios was explored by varying amounts of interlayer water. These experiments suggest exposing montmorillonite with 1 water of hydration (1W) to anhydrous $scCO_2$ under conditions relevant to geologic sequestration will not cause dehydration of the interlayer water and subsequent collapse of the interlayer spacing. In fact, these types of swelling clays will help maintain caprock integrity when exposed to anhydrous $scCO_2$. In contrast, the exposure of 2W montmorillonite to anhydrous $scCO_2$ promotes dehydration



In situ HXRD graphs depicting conversion of forsterite (F) into nesquehonite (N) when exposed to wet $scCO_2$ at 50°C 90 bar.

of the interlayer water resulting in a negative mineral volume change that could potentially induce permeability. Finally, in the present of wet $scCO_2$, the clay structure expands, indicating an incorporation of either water or $scCO_2$ into the interlayer.

Transformation reactions occurring with forsterite, $[Mg_2SiO_4]$, were examined in the presence of wet $scCO_2$. Under modest pressures (90 bar) and temperatures (50°C), water saturated $scCO_2$ was found to convert >70 wt% forsterite to a hydrated magnesium carbonate, nesquehonite ($MgCO_3 \cdot 3H_2O$) after 72 hours of reaction. However, comparable tests with $scCO_2$ at only partial water saturation (82%) showed a significantly slower carbonation rate with only ~30-39 wt% conversion. Further decreases in water content of the $scCO_2$ continued to reduce the extent of carbonation, until a critical moisture threshold (~30%) was crossed where forsterite no longer reacted in the presence of the wet $scCO_2$. Increasing the temperature to 75°C produced the anhydrous magnesium carbonate magnesite ($MgCO_3$), preceded by the intermediate phase of hydromagnesite $[Mg(CO_3)_4(OH)_2 \cdot 4H_2O]$. The contrasts in reaction rates, product formation, mineral stability, and water-content dependence demonstrated by in situ HXRD experiments with $scCO_2$ highlight the importance of these kinds of studies to help enable better predictions of the long-term fate of geologically stored CO_2.

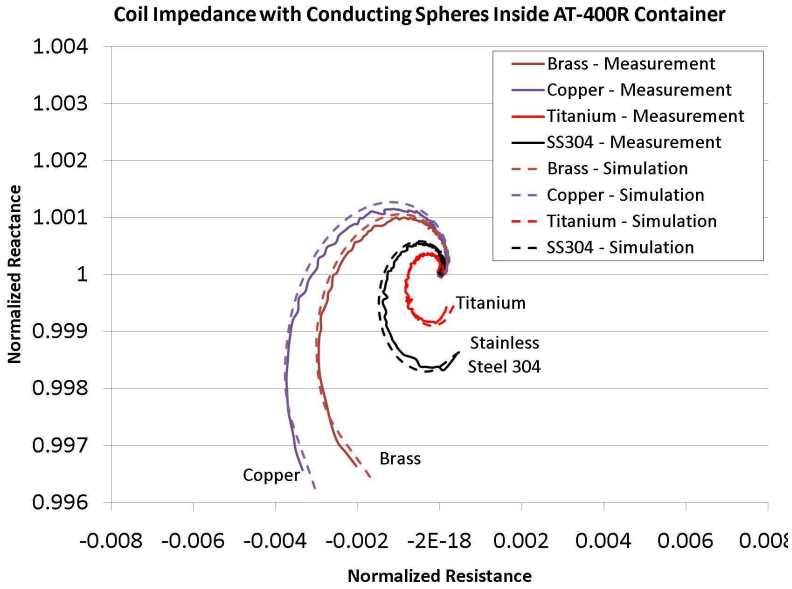
Proposed research activities for FY 2012 are designed to maximize the *in situ* capability primarily through conducting carbonation experiments. Efforts will focus on minerals such as feldspars, olivines, hornblendes, and phyllosilicates, which are important to targeted geologic and cap rock formations. Obtaining reaction kinetics associated with mineral carbonation during exposure to wet $scCO_2$ will be the primary objective. Additionally, efforts to expand this in situ HXRD capability through a second generation cell design are also scheduled.

Low Frequency Electromagnetic Interrogation Techniques for Container Content Signature Detection

Mark A. Jones, Kyle J. Bunch, Pradeep Ramuhalli, Daniel L. Stephens

◆ The objective of this project is to investigate the use of low frequency electromagnetic signals to detect concealed radiation threats in large, closed containers via the impedance signature produced by eddy currents induced in shielding materials. If proven viable, this technology will provide a means to perform rapid volumetric inspection of cargo containers to assist with detecting illicit nuclear materials. ◆

Research previously conducted at PNNL has demonstrated that the low frequency electromagnetic (EM) response of a sealed nuclear weapons storage container interrogated with an encircling coil is a strong function of its contents, and can be used to form a distinct signature which can confirm the presence of specific items. A natural extension of this research is to investigate the scalability and sensitivity of this technique to determine if it can be used to detect illicit nuclear materials concealed within large cargo containers. When properly normalized, the resulting signatures could provide material and geometric information that is complementary to conventional modalities such as radiation detection.



Normalized coil impedance signatures for a set of conducting spheres placed inside of an AT-400R nuclear weapons storage container.

This project will explore and quantify the use of low-frequency EM energy to interrogate large containers that contain radiation threats. Unknowns include the sensitivity of the signatures to variations in container and internal object size, composition, and geometry. We will determine which frequency range and sensor configuration maximizes the response of the coil system. Because experimental characterization of a complete set of these orthogonal parameters is unrealistic, we are using advanced finite element electromagnetic field simulation software to investigate the optimal detection configuration.

During FY 2011, we accomplished our intended tasks plus additional items. We validated the accuracy of the EM simulation software using coil impedance measurements for a set of conducting spheres placed inside a closed AT-400R nuclear storage container. The impedance values are normalized to the coil impedance with an empty container. Excellent agreement was obtained between the simulated and measured results. We also performed a simulation study on a hypothetical nuclear weapons storage container for a variety of operational parameters including coil size, interrogation frequency, container material properties, and internal object size. These results demonstrate that this methodology can enhance PNNL's capabilities for support of arms control treaty verification. A publication describing this simulation study is in preparation for submittal to the *Journal of Nuclear Materials Management*.

As part of the cargo container modeling, we performed EM simulations for intermodal cargo containers (IMCC) and air cargo containers (unit load devices) with metallic shielding geometries calculated to be necessary to conceal certain amounts of nuclear materials. Numerous three-dimensional models were analyzed for an 8 ft × 8 ft × 20 ft IMCC with various coil configurations, container material properties, and shielding material geometries and locations. The sensitivity of the coil response was quantified as a function of these parameters as well as the interrogation frequency. For carbon steel containers, interaction with the IMCC contents occurred for frequencies below approximately 500 Hz. Similarly, EM simulations were used to model the response of coils used to inspect an LD3 half-width lower deck air cargo container containing metallic shielding objects. For aluminum containers, interaction with the LD3 contents occurred for frequencies below approximately 200 Hz.

We have also completed a feasibility study to determine if the coil signature could be used as part of an artillery inventory management system. Simulations indicated that signals below 200 Hz may be used to penetrate closed carbon steel storage canisters and detect the presence of 155 mm

Howitzer artillery shells. Another activity for which significant progress was made in FY 2011 was the development of a circuit to measure the magnetic fields along the x, y, and z directions using state of the art anisotropic magneto-resistive sensors. Measurements of the magnetic fields outside a closed AT-400R nuclear storage container interrogated by an encircling coil are being used to determine if magnetic field mapping can provide additional information regarding the internal contents of the container.

Plans for FY 2012 project progress include additional development of models for specific applications to optimize the configuration and define the knowledge limits of methods for these scenarios. We will also continue the magnetic field sensor circuit development and magnetic field measurements.

Neutron Signature Detection Requirements for Identifying Warhead Configurations

Robert I. Scherpelz, Jacob M. Benz, Bryce A. Greenfield, David V. Jordan

◆ Agreements for the control of nuclear weapons depend on verification measurements. This study investigates the detection of neutron signatures for identifying warhead configurations, which could provide reliable and accurate discrimination between different configurations. ◆

Arms control verification measurements commonly exploit the gamma-ray signatures of nuclear warheads. The material in the warheads emits neutrons in addition to gammas, and neutron signatures have not been commonly used for verification measurements. This project is employing a combination of calculations and measurements to study the feasibility of using neutron signatures. The study will result in a coherent and defensible scientific basis for assessing the ability of a practical neutron detection system to extract useful information from warhead neutron signatures and to furnish guidelines for future research and development to meet our warhead counting needs. A system that can identify warhead configurations based on its neutron signature would be a significant addition to our nation's set of tools supporting arms control.

Our team has constructed detailed MCNP5 models for five different U.S. weapons types. These five items have been placed within various shielding materials and configurations to determine their effect on the emitted neutron spectrum. Currently, 35 different configurations with these items have been investigated. Potential intervening materials, including structural materials, high explosives, and various fissile materials were all considered for inclusion in the potential configurations to be analyzed. Careful analysis and discussions with experts were used to develop a modeling matrix to track the many potential scenarios and configurations of interest.

The results from the 35 configurations were then used to drive the methodology for constructing various scenarios in which an item's signature could be compared against other similar and dissimilar items and configurations. During this portion of the project, a wide array of configurations and materials were analyzed. The study then constructed a set of generic pit-like models that were created to simulate other nuclear weapon configurations, which may or may not resemble the five items mentioned above. These generic pit-like models will be used in FY 2012 to investigate material effects on the neutron spectrum.

Our project addresses application of readily-deployed technologies for neutron detection. We model the spectral response of a notional neutron detector to each weapon configuration and test for count-rate and shape differences between different inspected items. We have developed a set of detector response modeling and neutron energy spectrum discrimination tools that incorporate a chi-squared test of spectral shape differences. Detector types currently supported include neutron-proton-recoil (i.e., liquid scintillator), neutron time-of-flight, and Bonner sphere spectrometers. We account for detector size, standoff, and intrinsic efficiency, and reasonable collection times. We compute the probability that the spectral responses from different source terms can be reliably distinguished from each other using a given detector type, under the specified measurement conditions.

Results of the modeling study suggest that different configurations of weapon and shielding are readily discriminated from one another using existing neutron detection technology and practical measurement times. In almost all cases studied, the gross-count response in the fast-neutron portion of the emitted spectrum suffices to reliably distinguish one configuration from another. In the remaining cases, differences in shape of the detected fast-neutron energy spectra clearly distinguish the configurations. The feasibility of extracting "intrinsic" signatures of device composition and/or shielding from the detected neutron energy spectrum (i.e., those spectral features or metrics accessible without relying on change-detection comparison against a template) is still under examination as FY 2011 concludes.

During FY 2012, we will test the results of our calculations by performing neutron measurements. We will use a neutron spectrometer with the general characteristics of one of the types that were investigated in the discrimination analysis in FY 2011. Next, we will use neutron sources in the laboratory, along with neutron moderators and shields, to determine the ability to discriminate between the neutron signatures of the configurations. We will compare the measurements to the results that were predicted by our calculations. The final result will be recommendations on the effectiveness of neutron spectrometers to detect the neutron signatures from weapons configurations and determine whether the neutron signatures can be used to discriminate between a declared configuration and a potential spoof.

Optical Upconversion for Passive and Active Millimeter and Terahertz Imaging

Douglas L. McMakin, Bruce E. Bernacki, Leonard S. Fifield, David M. Sheen, A. Mark Jones, Mark C. Phillips, Jonathan D. Suter

◆ Our objective is to develop active polymer-based electro-optical components to upconvert millimeter-wave energy to optical frequencies to exploit optical signal processing techniques. ◆

Millimeter-wave imaging can see through many obscurants opaque to optical imaging but with lower spatial resolution than optical approaches. Synthetic aperture imaging can increase spatial resolution using an array of small antennas but is challenging with conventional millimeter-wave technology. Synthetic aperture imaging using optical upconversion exploits the use of compact and low-loss telecom fibers (1000 times lower loss per meter compared to millimeter-wave waveguide), efficient optical oscillator generation using high power telecommunications lasers, and low-loss fiber distribution of the local oscillator. Polymer-based modulators offer better performance (wider modulation bandwidth into the sub-THz region and lower $V\pi$), potentially lower cost, simpler fabrication methods as well as compatibility with integrated circuit technologies compared to the more traditional lithium niobate construction.

This project will design, build, and demonstrate an optical modulator combined with an optimized millimeter-wave antenna to upconvert received millimeter-wave energy directly into an optical signal representation. The optical signals can be routed, combined, and processed with reduced signal loss, size, weight, and power compared to conventional millimeter-wave components to enable compact and higher resolution all-weather synthetic aperture millimeter-wave imagers essential to detect the movement and production of weapons of mass effect.

At project completion, we will have developed a polymer system (cladding-core-cladding) suitable for an active electro-optical modulator, fabricated a phase modulator, and demonstrated the upconversion of millimeter-wave signals to their optical representation under modulation of a millimeter-wave signal. The project would provide millimeter-wave components that permit all-optical processing of millimeter-wave signals at the output of the system's antenna. The parameterized millimeter-wave signal would preserve the power, spectral response, and polarization state of the incident beam. Additionally and specifically, the ability to generate a stable optical carrier will enable very stable synthetic aperture systems that can make possible mobile imaging systems with reduced size, weight, and power. Our outcomes are anticipated to include design and fabrication of a 94 GHz (W-band) optical modulator demonstrated use of an optical modulator to upconvert 94GHz millimeter-wave signal to telecom wavelength and collection of passive millimeter-wave images; and peer-reviewed publications describing novel achievements.

For FY 2011, we focused on several objectives. Initially, we reviewed the scientific literature to determine the best approach and polymer choices. Next, we formulated the design and numerical modeling of candidate waveguide designs and developed a robust fabrication approach, which included the identification and synthesis of a compatible polymer system for creating an active electro-optical modulator. Finally, we worked on the fabrication and characterization of a passive wave-guide using the candidate material system. A basic optical waveguide consists of a core surrounded by cladding layers.

Our polymer system consists of a core or active layer of a thermoset polymer. The cladding layers consist of a commercially available thermally cured epoxy. The waveguide structure is formed by spin coating each layer on a silicon wafer, patterning of the waveguide channel, followed by poling the randomly oriented chromophore molecules.

In FY 2012, we will use the polymer system to fabricate waveguides by spin coating and patterning a channel to demonstrate lateral confinement using either photo-bleaching or lithographic photo resist patterning. Either approach can be accomplished using photo masks in conjunction with the ultraviolet flood source purchased in FY 2011. We will also pole the waveguide by patterning metal contacts and applying an electric field or using a corona poling approach. Lastly, we'll demonstrate phase modulation of an optical signal using the fabricated waveguide modulated by a millimeter-wave signal.

Biological Sciences

Application of a Systems Biology Approach to Understanding Protein Function

Karin D. Rodland, Richard E. Jacob, Simon H. Kahan, Norman J. Karin, Helen W. Kreuzer, Richard E. Weller, Aaron T. Wright, Richard C. Zangar

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

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

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

In FY 2009, we refined the ability to link protein structure with function, which required more research to explain molecular theory and explore sophisticated computational methods for antiferromagnetic model compounds. We succeeded in defining the conditions for sustained release of immunoglobulin G from functionalized mesoporous silica particles under physiological conditions, establishing the proof-of-principle for using functionalized mesoporous silica particles in cancer therapy. Continuing into FY 2010, we validated a system-theoretic model for integrated cell signaling that captures all of our experimental observations. These results were used to refine the mechanistic model for oscillations and to validate predictions with targeted experiments. During these previous two years, systems biology applications successfully developed under our project include the following successful efforts:

- Improved modeling and simulations capability for biological effects of nanoparticles and dynamic cellular processes
- New functional imaging capabilities for respiratory function using unique Magnetic Resonance Imaging capabilities
- Development of chemical probes for activity-based protein profiling of metabolic enzymes
- Development of in vivo and in vitro model systems for chemical, biological, nuclear, and radiological countermeasures and surveillance
- Development of assays for protein modifications associated with oxidative damage.

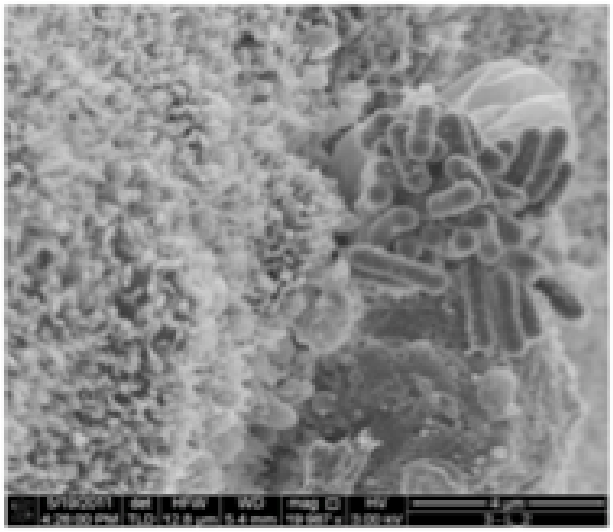
Some of the specific tasks undertaken in FY 2011 and their outcomes are briefly described below.

Develop an activity-based protein profiling capability for mitochondrial function. We designed and synthesized activity-based probes for nitric oxide synthases. In addition, we measured enzyme activities using chemical probes in the mitochondria and cellular membranes of multiple cell types.

Predict the effects of novel nanomaterials on biological systems. Under this specific task, we performed the following: developed computational models to describe the fundamental interactions between proteins and nanomaterials; developed logistic regression framework for interpreting embryonic zebrafish nanoparticle data, addressing incomplete data entries, and assessing statistical significance between assays; and developed initial regression tree models for nanoparticle data analysis and toxicity prediction.

Develop and test bio-nanomaterials for delivery of proteins and lipids for bioengineering of complex systems. We leveraged the ability to predict biological responses to peptide growth factors and lipids (e.g., lysophosphatidic acid [LPA]) to develop a sustained release hydrogel system that can predictably heal bone defects. Specifically under this task, new surgical capabilities have been established that enable the investigation of nanomaterials as aids to bone regeneration, and experimental data demonstrating that the postulated bone healing agent (LPA) elicited a clear stimulation of blood vessel formation (angiogenesis) in cranial defects were generated. Use of high-resolution MRI to measure blood formation in live laboratory rodents also was successfully demonstrated.

Development of three-dimensional human intestinal co-culture with commensal intestinal bacteria. The ability to culture a community of host cells (human intestinal epithelial cells) and commensal bacteria (*Lactobacillus reuteri*) was successfully demonstrated in a three-dimensional culture system. This established a capability to study complex communities involving prokaryotic and eukaryotic cells in an environment simulating the intestinal tract.



SEM image showing successful colonization of intestinal brush border cells by Lactobacillus reuteri.

PNNL has a long-term commitment to offering the scientific leadership and technology needed to provide a quantitative understanding of multicellular biological systems from microbial communities to humans. We have broken ground by shifting biology from a descriptive to a predictive science that allows us to predict, manipulate, and potentially design multi-cellular systems and bio-inspired solutions for bioenergy, contaminant fate and transport, carbon sequestration and global climate change, and human health.

Aspergillus niger as a Platform for exploitation of the Advanced Biofuel Producing Potential of Filamentous Fungi

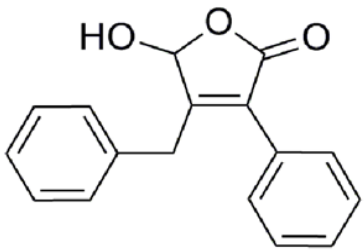
Kenneth S. Bruno, Brigette K. Ahring; Afrab Ahamed (WSU Tri-Cities)

◆ This project will result in the development of new tools that will provide the means necessary for discovery of novel polyketide hydrocarbons that can be produced by fermentation. ◆

A number of pathways to energy-dense, infrastructure-compatible hydrocarbon biofuels and biofuel precursors are possible. Three biological routes to these compounds are through fatty acid, isoprenoid, and polyketide synthesis. Fatty acids consist of long chains of hydrocarbons readily converted to fuels such as diesel. Isoprenoids (or terpenoids) are secondary metabolite compounds whose natural material has been produced for decades in antibiotics and therapeutic agents. With the advent of genomics and advances in molecular biology, high levels of secondary metabolite production have been sought as a source of advanced biofuel. Like isoprenoids, with 10 to 50 carbon atoms that vary in degree of oxygenation (hydroxyl and ketone groups) saturation and cyclization. Currently, two private companies are engaged in this type of research, but very little effort is focused on polyketides as a source of hydrocarbons. Traditionally, filamentous fungi have been a valuable source of secondary metabolites, but they have yet to be explored as potential biofuels.

Our goal will be to build a flexible "chassis" that will allow us to determine rapidly the key genes found in native hydrocarbon producing organisms and express these in a fungal production system with an extensive track record of industrial usage. We will amplify the polyketide synthase (PKS) genes from available fungal genome sequences and constitutively express them by homologous integration into *Aspergillus niger*. Compounds produced by these strains will be analyzed by solid phase micro extraction (SPME) and the structure of the compounds determined by mass spectroscopy and nuclear magnetic resonance. Molecules with desirable properties will be selected for optimization to increase yield. We also aim to discover novel polyketides from filamentous fungi, which could have a tremendous impact on biofuels. If polyketides can be made from complex biomass without preliminary processing into simple sugars, we will have developed the capability for advanced biofuels produced through fermentation.

During FY 2011, we successfully generated strains that express metabolite genes from other fungi. A single gene from the species *A. nidulans* was fused to an inducible promoter. We demonstrated that this single gene can be used to generate the compound microperfuranone. This construct was placed in *A. niger* during a simultaneous integration of a mutation at the albA locus. The resulting strain has a relatively clean metabolic profile when examined by liquid chromatography. Induction of the transgene results in a very clear peak that is easily distinguished from compounds generated by the native strain. This demonstrates that this platform can be used to generate novel compounds and do so in a manner that facilitates analysis.



Microperfuranone compound produced by taking a gene from A. nidulans *and expressing it in* A. niger.

We also successfully developed and tested a means to perform metabolite analyses using gas chromotagraphy. Extracts from the strain detailed above were subjected to analyses using solid phase micro extraction. We were easily able to delineate the presence of a novel peak not present within control samples. Development of this tool was a goal for our project during FY 2011. This approach can greatly accelerate the throughput in and allow for the rapid screening of transformants. Additionally, a new set of expression vectors were generated that will allow for the rapid integration of other novel enzymes capable of producing hydrocarbon compounds. These expression vectors allow us to produce the promoter fusions in two simple steps. Genes can be amplified from the target organism and fused into the vector, which in turn can be directly transformed into *A. niger*.

In FY 2012, we plan to express PKS genes from fungal species from several genera using the vectors that were developed in FY 2011. We will adapt the SPME to higher throughput analysis to support rapid screening. Though we have already demonstrated the functionality in FY 2011, it will be put into practice for the upcoming year. Additionally, we will analyze expression of these compounds in liquid cultures that are also generating primary metabolites.

Characterization of Signaling Networks in Single Cells

Bryan E. Linggi, Nitin Agrawal, Shyretha D. Brown

◆ We propose experiments to characterize signaling networks in single cells using microfluidic systems to decrease necessary sample input and increase molecular measurement resolution. Characterization and enumeration of the variability of these signaling network "states" will greatly advance our understanding of cellular responses and the behavior of cell communities. ◆

Cell communities exhibit complex responses to changes in their environment. Studying molecular changes (e.g., RNA and protein) associated with these changes is likely to improve the ability to predict the behavior of these communities and engineer them for human benefit. However, traditional assays that measure these changes at the population level obscure the underlying cell to cell variability that exist even in homogenous (clonal) population. By understanding the differences in signaling at the level of the cell, rather than cell population, we can begin to unravel the apparent heterogeneity in cell response (so called "rare-events") that mediate many biological processes.

Our conceptual understanding of the mechanistic basis for cell responses has been limited by the inability to measure molecular changes at the single cell level. A few elegant studies have demonstrated that single cell measurements are necessary to capture the dynamics that are occurring at the phenotypic (i.e., cell response) level. Our own studies have identified a great diversity of cell responses that cannot be explained by population based measurements and models. Thus, there is a critical need to measure molecular changes at the single cell level to understand the inherent variability amongst cells and appropriately link them to cellular behavior. In accordance with these issues, the DOE has identified single cell analysis as a critical technology for enabling systems biology.

A specific and critical biological question that will be addressed by these studies is "how different are cells in a 'clonal' population?" This is a simple but fundamental question that has not been addressed due to technical limitations (i.e., measuring population averages). In some cases, the relative levels of selected proteins within a cell have been measured using flow cytometry and related to the phenotypes of those cells. However, the applicability of this approach is limited because it requires exceptional antibodies to the protein(s) of interest and the number of proteins that can be analyzed for a single cell is limited by the number of channels on the flow cytometer.We use messenger RNA (mRNA) as a readout for signaling states because of the technical benefits it offers: RNA measurements are mediated by nucleic acid hybridization, which is very specific, and RNA measurements are very sensitive due to the ability to amplify RNA templates using polymerase chain reaction. Furthermore, we will be able to monitor the signaling activity by measuring the mRNA level of downstream transcriptional targets, thus using them as "surrogates" for activated signaling proteins.

During FY 2011, we optimized multiple approaches to capture and analyze single cells using microscopy and microfluidic devices. The first technical accomplishement was identifying the optimal conditions for amplification of minute amounts of RNA. Using a limiting dilution of starting RNA from a standard sample, we were able to detect the transcript expression of GADH from the equivalent of 0.5 cells. This important step validates the ability to measure gene expression following single cell capture. We also created several microfluidic designs to capture cells. Cells were typsinized, loaded into these devices, and were captured using a variety of different "capture wall" geometries. Our optimization experiments identified optimal flow rates and geometries required. Additionally, we designed devices that allow for precise control of two-fluid interfaces. This system will be used to selectively lyse single cells that are part of an arrayed population of cells. This increases the throughput of the system. Flow simulations were confirmed by experiments.

The third main area of development was the creation of cells containing fluorescent reporters for cell state. During FY 2011 we created four different clonal populations (single cell derived) cell lines for future use. One contains a red fluorescence marker of cell cycle progression called a FUCCI reporter. The other three are green fluorescent reporters of transcription factor activity (AP1, STAT, SRF). We additionally combined the green and red reporter systems to allow dual color imaging for quantitating cell cycle and transcription factor activity in a single cell.

In FY 2012, we will isolate RNA from single cells (under a control and EGF stimulted condition) using the technologies developed in FY 2011. This will involve single cell capture, lysis, amplification, and RNA-seq. Libraries from single cells will be barcoded and multiplexed for the RNA-seq run. The data derived from this experiment will be the first to identify coregulated genes at single cell resolution. Also planned is the single cell capture on micropatterned "adhesive islands." This will allow us to spacially and geometrically constrain the cells and then analyze the expression of genes and the progression of the cell cycle following changes in the interactions with the external environment (e.g., EGF, substrate).

Combining Proteomic Technologies to Create a Platform for Spatiotemporal Enzyme Activity Profiling

Susan D. Wiedner, Aaron T. Wright, Ellen A. Panisko

◆ We seek to combine the proteomic technologies of activity based protein profiling (ABPP) and subcellular proteomics. Individually, these two technologies study different "fractions" of the proteome and in combination would provide spatiotemporal information of the functionally active proteome. ◆

ABPP and organellar proteomics are techniques used in proteomics to decrease the complexity of the natural cellular proteome, which often contains thousands of proteins. Activity-based protein profiling isolates the active portion of the proteome by tagging functionally active enzymes with chemical activity based probes. By contrast, organellar proteomics reduces complexity by focusing on the proteome of subcellular compartments. Combining ABPP and organellar proteomics into the spatiotemporal enzyme activity profile (STEAP) will provide information about the functionality of active proteome on the organelle level. This information will help elucidate on a cellular level fundamental biological processes such as protein translocation, signaling, and cellular response to environmental stress. The STEAP platform will be used in systems biology to compare biologically relevant proteomes such as diseased systems. The following describes progress made in developing STEAP to investigate spatiotemporal enzyme activity of fungi and host response to the lung disease invasive aspergillosis (IA).

IA is caused by the pathogenic filamentous fungus *Aspergillus fumigatus* and is a deadly, costly infection often found in immunocompromised patients. To date, there is no definitive diagnostic test for IA except postmortem autopsy, yet early detection and diagnosis is critical. Further, a better understanding of the virulence factors of *A. fumigatus* and how host enzymatic function responds to infection would increase the potential to find ways to combat this disease. Our goal is to develop and use STEAP to investigate a host response to infection with *A. fumigatus* on a subcellular level and to find enzymatic biomarkers for infection.

Our plan in FY 2010 included studying *A. fumigatus* with ABPS using liquid chromatography-mass spectrometry (LC-MS). Novel activity based probes that target phosphatases, serine hydrolases, and glutamine synthetase enzymes were synthesized and evaluated for ABPP. Sample preparation, LC-MS analysis, and bioinformatics data analysis were used to identify the tagged enzymes. The active proteome of *A. fumigatus* was compared with two closely related non-pathogenic filamentous fungi species: *A. clavatus* and *Neosartorya fisheri*.

During FY 2011, a new general vinyl sulfonate activity-based probe was synthesized in four steps from commercially available material. For detection, the probe labeled enzyme is attached to a fluorescent indicator via a copper catalyzed [3+2] cycloaddition. We visualized the tagged proteins using 1D-SDS PAGE. Test labeling studies showed that enzymes in a mouse liver microsome proteome were tagged, and LC-MS analysis confirmed that the probe targets nucleophilic active site amino acids in diverse enzyme classes. To investigate possible virulence factors using general ABP, *A. fumigatusi*, the non-pathogenic *A. clavatus*, and *N. fisheri* were grown under various conditions that subjected the fungus to human protein to evaluate enzyme activity in an infection environment. Initial gel-based analysis of labeled lysed biomass showed differences between the three fungi in the presence and absence of human serum or the lung epithelial cell A549. LC-MS analysis of labeled samples is pending and will be completed before FY end.

Also during FY 2011, *A. fumigatus* was cultured and grown to produce fungal biomass for ABPP labeling studies. For analysis of the *A. fumigatus* proteome, the biomass was lysed and homogenized using a bead beating blender to disrupt the fungal cell wall. Once lysed, standard biological separations and mass spectrometry group sample preparation protocol was used to prepare samples for LC-MS analysis. The data collected will generate an accurate mass and time (AMT) tag database to identify probe labeled proteins in subsequent ABPP labeling studies. *A. fumigatus* biomass was processed and fractionated for ABPP labeling, and global and light membrane fraction were labeled with multiple probes to target PTP, P450s, serine hydrolases, and glycoside hydrolases. Initial analysis by 1D SDS-PAGE showed that the probes have tagged enzymes within these proteomes.

During FY 2012, we will study *A. fumigatus* labeling of infected A549 cells and mouse macrophage cells after completion of the *A. fumigatus* active proteome analysis in the presence of human proteins, which will provide biomarkers of infection for the fungus, enabling possible detection of these proteins in the infection model. We will also fractionate and label infected cells to develop a spatiotemporal enzyme activity profile of IA. Future development of this platform involves the design and synthesis of new activity-based probes that will be based on known fungal inhibitor scaffolds to investigate their mode of anti-fungal activity. Nitrogen fixation pathways will be targeted by derivatized amino acids.

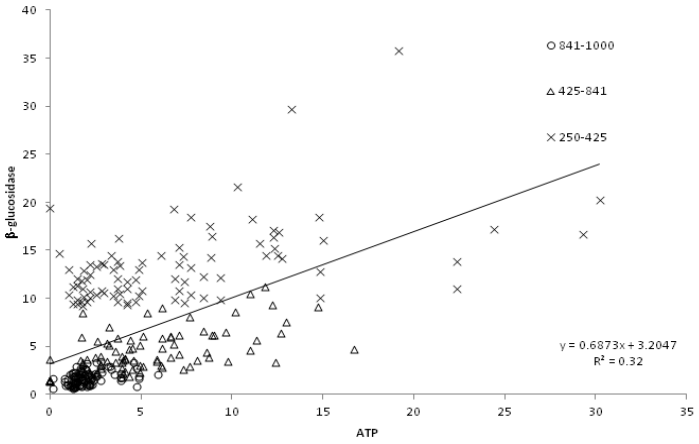
Community Diversity and Functional Redundancy of Cellulytic Microbial Communities in Soil Aggregates

Vanessa L. Bailey, Lee Ann McCue

◆ An understanding of the role of natural microbial communities in the global carbon cycle is fundamental to our ability to mitigate the effects of greenhouse gases. To gain this knowledge, we must bridge the current knowledge gap between the community *structure* (who's there?) and the *functional potential* (what are they doing?) of microbial communities. ◆

Soils are highly complex systems in terms of their composition, dynamics, and heterogeneity, with an estimated 10^9 bacteria and up to 1 km of fungal hyphae in 1 g of soil. Aggregates are the building blocks of soils, and highly stable individual microaggregates (less than 250 μm diameter) bind together to form more dynamic (i.e., shorter-lived), larger (up to and greater than 2 mm diameter) aggregates. These individual and compound aggregates form different habitat types and are likely to feature different microbial community structures and functions. Additionally, the smaller, stable microaggregates are the location of the most protected, stable carbon in the soil. As these different types of soil aggregates are what comprise the fabric of an intact soil, it is clear that the fine-scale aggregates exert a strong influence on the behavior of the whole soil.

With recent advances in DNA sequencing technologies and microscale enzyme assays, it is now possible to study the diversity of soil microbial communities, activities of community members, functional redundancy of the community as a whole, and resiliency to perturbation at the fine scale of soil aggregates, nominally sorted into four size classes (less than 250 μm, 250 to 425 μm, 425 to 841 μm, and 841 to 1000 μm). The soil carbon cycle is complex and diverse; therefore, we focused on the metabolism of cellulose, the most abundant natural biopolymer on the planet. Enzyme assays have been developed for bulk soils, allowing the study of the entry of cellulose-derived carbon into the soil through the action of microbial cellulases. Examination of soil at fine scales (such as individual aggregates) requires developing highly sensitive fluorescence-based cellulase enzyme assays to reveal the functional capability of the community and the resiliency of the community to perturbation.



Correlation of β-glucosidase activities and ATP g-1 soil in 90 aggregates assayed individually and consecutively on the same individual aggregates. Aggregates are 250-1000 μm in diameter, reported together (P<0.001).

DNA pyrosequencing data for the 16S ribosomal DNA from individual soil aggregate samples revealed that the species richness of an aggregate has been thoroughly sampled with only a few hundred sequences. Analysis of the β-diversity of the aggregates shows that each aggregate has a relatively unique community and is dominated by only a few different microbial types, with these dominant microbes varying between aggregates.

Microscale enzyme assays to measure cellulase activity of individual aggregates were carried out in FY 2010. Classical β-glucosidase assays were scaled down to reactions in a few microliters with fluorescent detection of the reaction products. These microscaled assays showed that the per-volume enzyme activities in the smallest aggregates varied far more than the per-volume biomass of those aggregates, suggesting that either the smaller aggregates were favoring microbial communities that were more responsive to substrate additions or that potentially active extracellular enzymes were protected within the aggregates. The microbial biomass measurements from within these aggregates were also not correlated to the activity of other enzymes (lipase, β-N-acetylgluco-saminidase). In FY 2011, similarly assayed aggregates were classified into "high" and "low" β-glucosidase activities, and these aggregates sent for sequencing. Comparison of the microbial communities in these two categories should allow us to link microbial community function more closely with microbial community structure in a natural, complex ecosystem.

During FY 2012, we will analyze the sequences collected in the high and low activity experiment. We will also analyze data collected on aggregates exposed to ^{13}C-labelled cellulose during a 12-week incubation to identify the cellulytic members of the soil microbial community. This research has developed new approaches that are now being used to link community phylogenetic composition with functional potential.

Correlative High Resolution Imaging and Spectroscopy to Characterize the Structure and Biogeochemical Function of Microbial Biofilms

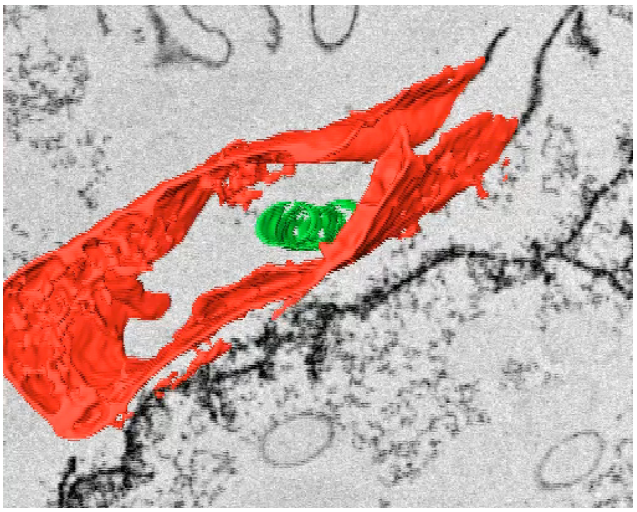
Matthew J. Marshall, James K. Fredrickson, Alice C. Dohnalkova, Erin A. Miller, Zihua Zhu

◆ This research aims to develop correlated capabilities for state-of-science imaging, compositional analysis, and functional characterization of microbial biofilms, and to understand biofilm influences on biogeochemical processes such as the fate and transport of radionuclides in the subsurface or carbon sequestration. ◆

In both natural and engineered environments, the majority of microorganisms live in structured communities termed biofilms. In addition to microbial cells, biofilms are composed of a poorly characterized organic matrix commonly referred to as extracellular polymeric substance (EPS) that may play roles in facilitating microbial interactions and biogeochemical reactions including extracellular electron transfer (EET). Using high-resolution electron microscopy imaging, a highly hydrated, three-dimensional EPS was produced during microbial metal reduction. The juxtaposition of EET proteins and nanoparticulate-reduced metal suggested that EPS played a key role in metal capture, precipitation, and possibly EET. Understanding how biofilm EPS interacts with inorganic substrates (i.e., metal ions and mineral surfaces) connects the molecular-scale biogeochemical processes to those at the microorganism-level and provides insight into how microorganisms influence larger, pore-scale processes.

Using a multi-faceted, multi-scale approach of imaging and analytical techniques to elicit the complex microbial and biogeochemical interactions, biofilm communities will be surveyed in its nearest-to-native state. The following techniques will be used to interpret biofilm community structures and gain knowledge of EPS composition: confocal laser scanning microscopy and cryo light/fluorescence microscopy with soft x-ray tomography. Conventional and cryogenic electron microscopy capabilities will be correlated with synchrotron-based computed microtomography, x-ray fluorescence micro-imaging, scanning transmission x-ray microscopy, and nano-secondary ion mass spectroscopy to produce high-sensitivity, element-specific distributions which correspond to electron microscopy images and three-dimensional reconstructions of the biofilm. Together, these techniques will provide detailed, high-resolution visualizations and compositional data of biofilms in their nearest-to-native state as they influence local biogeochemical reactions in their environment.

During FY 2010, our perceptions of the size of nascent reduced uranium (UO_2) nanoparticles have been limited by the resolution of the high-resolution electron microscopy. This was confirmed when x-ray absorption spectroscopy found that average UO_2 nanoparticle size was smaller than observed using electron microscopy, suggesting that properties such as reoxidation and transport may be influenced. The recent addition of an aberration-corrected Titan scanning/transmission electron microscopy-enabled atomic-scale discovery of biogenic UO_2 nanoparticles and the observation of nanoparticles smaller than 1 nm. Another important step toward understanding the nanometer-scale interactions of UO_2 with EPS involved the serial sectioning and three-dimensional reconstruction of cells and the EPS matrix associated with UO_2. Reconstructions of *Shewanella* cells and the UO_2-EPS matrix are in progress.



Amira three-dimensional reconstruction of Shewanella *cell and EPS matrix associated with UO_2. The cell can be seen in close proximity with UO_2-EPS.*

X-ray microtomography can provide three-dimensional maps of pore structure on complex matrixes such as soil, but obtaining sufficient contrast to image low-Z organic material against a higher-Z substrate may make detecting biofilms difficult. In initial x-ray experiments, we used three physically distinct signatures – absorption, phase, and scatter – for imaging biofilms on complex matrixes. The complex matrixes included a hollow-fiber, a Bio-Sep bead, and soil aggregates. Results were obtained on the characteristics of several phase contrast methods: absorption/propagation-based, Fourier x-ray scattering radiography (single grating), and Talbot interferometry (double grating with phase stepping) with tomography data acquisition. Analysis of the data suggested that Talbot interferometry produced a line visibility of

approximately 30% as the absorption grating was phase-stepped past the phase grating, leading to improved signal in phase and scatter. In all analysis, dried (or collapsed) biofilms were difficult to distinguish against the higher-Z substrates. This suggested that thicker biofilms may be required. Additionally, contrasting agents such as ruthenium or osmium may help to distinguish between organic materials and substrates.

Our combination of microscopy and x-ray experiments has poised us to narrow significantly the technology gap between electron microscopy and x-ray capabilities during FY 2012. The first year x-ray microtomography and electron microscopy reconstruction experiments have will allow us to construct higher-quality three-dimensional data sets. Through the use of contrasting agents and data collection at additional synchrotron beam lines, we expect to gain important chemical and elemental information from hydrated biofilms. This knowledge will be integrated into three-dimensional data as they become available.

Development of Functionalized Nanoporous Materials for Bioenergy and Biomedical Applications

Chenghong Lei, Baowei Chen, Tsz Kin Tam, Xiaolin Li, Yuehe Lin

◆ We propose to develop a transformational material platform allowing high loading density of active biomolecules based on functionalized nanoporous materials for bioenergy and biomedical applications. ◆

There is a history of biomolecule immobilization using solid supports. Using conventional immobilization methods, the specific activity of immobilized enzymes is usually less or much less than that of free enzymes in solution prior to the immobilization. In general, the low efficiency of conventional immobilization approaches is mainly because of the low available surface area of the supports, small pore sizes, non-open pore structures (encapsulation), and harsh conditions of cross-linking/polymerization, which result in some protein denaturation and concomitant activity loss. Mesoporous silicas have unique properties, including low toxicity, open nanoporous structures, large surface area (up to 1000 m^2/g), tunable pore size, and flexible surface chemistry for high loading and for optimizing the biomolecular interaction and delivery.

In this project, we are developing functionalized mesoporous silicas (FMS) and other alternative nanomaterials for highly loaded and highly active biomolecules for targeted bioenergy and biomedical applications and accordingly enhance PNNL's capabilities in biological sciences, bioenergy, environment, and national security. We will build a transformational technological platform to allow for high loading density of biomolecules with high efficiency of biomolecular activity based on functionalized nanoporous materials. Thus far, our progress during FY 2011 in the following tasks is detailed below.

Development of functional nanoporous materials. Mesoporous silica with the same adsorption but different desorption pore sizes and different surface areas and pore volumes were synthesized by adjusting hydrothermal aging temperatures. We elucidated the effects of intramesoporous structure on loading proteins and enzymes. Innovatively, we reduced particle size of mesoporous silicas from ~15 μm to ~2 μm in aqueous solution by non-destructive powderization, where the mesoporous structure was still maintained. The silicas with reduced particle sizes allowed protein loading densities increased by more than 40%. Finally, we developed a flow induced gelation approach to enable entrapment of enzymes into gel scaffolds, which is independent of the enzyme size and structure and is functionally noninvasive and preserves the integrity and directional homogeneity of the enzyme surface microstructure.

Bioenergy and biomedical applications based on functional nanoporous materials. We entrapped four essential enzymes, the needed enzyme cascade involved enzymatic conversion of CO_2 to methanol in FMS. The enzymes included carbonic anhydrase, formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase. All enzymes were highly active and functional in FMS with large loading density. We also explored electrochemical approaches to regenerate electron donor NADH needed for the enzyme cascade reaction. Next, we tested local release of antibodies (anti-CTLA4, anti-CD3, and anti-CD28) from FMS for cancer immunotherapy on a mouse melanoma model. Compared to the free antibody, the FMS-antibody injected at the tumor site, as expected, showed much higher concentration of released antibody at the tumor site but much lower concentration in blood. FMS-based local release of antibodies showed very promising prospect to be more effective, less side effects and reduced cost compared with conventional systemic administration of antibody drugs.

We found that under different physiological conditions, organophosphorus acid anhydrolase (OPAA) can be stockpiled in FMS, be instantly released when needed for acute responses, and gradually released from FMS over time for complete recovery. The in vitro results in rabbit serum demonstrate that OPAA-FMS and released OPAA can be used as the preventive measure against the nerve agents. By flow-induced gelation, we also found that gel scaffolds can contain a sufficient amount of trapped interstitial water to form a more stable aqueous microenvironment to maintain enzyme bioactivity. We tested the resulting enzyme nanocomposites for biosensing application. Thus far, our project has produced two journal articles and submittal or preparation of three additional papers.

Our FY 2012 project goals will be to continue developing functional nanoporous support for bioenergy applications, integrating enzymatic approach for conversion of CO_2 in functional nanoporous materials with electrochemical regeneration of the electron donor to produce useful compounds. We will also proceed our development of the functional nanoporous support for loading biomolecules for biomedical applications, including FMS-immunologically active biomolecules for cancer immunotherapy for both ovarian cancer and melanoma models and FMS-hydrolysis enzymes as the preventive measures against the organophosphate nerve agents.

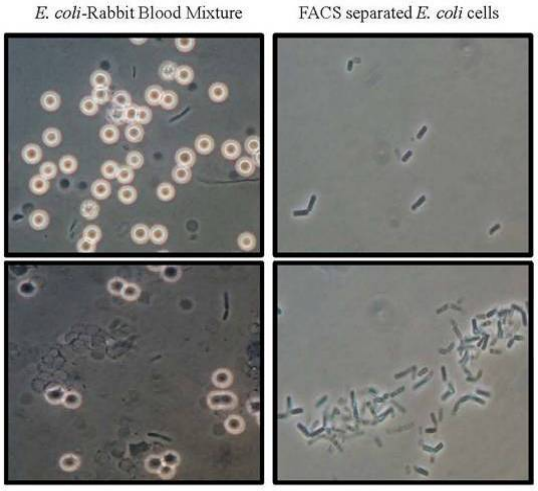
Distinguishing *Yersinia pestis* from Natural Host and Laboratory Culture

Helen W. Kreuzer, David S. Wunschel, Christopher J. Ehrhardt, Douglas C. Duckworth

◆ The goal of this project is to produce the organism that causes plague, *Yersinia pestis*, in a natural host (the rat) in laboratory cultures and compare chemical and biochemical signatures of the various samples to develop means of distinguishing the two cases. ◆

A topic of interest to the homeland security, intelligence, and law enforcement communities is distinguishing natural occurrences of pathogens (e.g., from death of an infected animal) from the release of laboratory-produced organisms. Chemical and physical analysis of the material can likely distinguish the two possibilities if genetic analysis cannot provide a conclusive answer. Like other disease agents, *Y. pestis* occurs in nature in the United States and elsewhere. If its presence is detected, it is important to determine whether the detected organisms are naturally occurring or were deliberately released. This issue has caused several high-profile false alarms in the air monitoring program for biological agents Biowatch, for example. A number of confounding variables will need to be examined to demonstrate the feasibility of this approach.

This project seeks to investigate the chemical signatures of pathogen that would allow for a "naturally occurring" isolate to be distinguished from a laboratory cultured organism. We are studying the key pathogen *Y. pestis* produced in a natural host and in culture media and comparing chemical and biochemical signatures of the various samples. Specifically, we are using an experimental rat model for producing the *Y. pestis* cell mass. With this path, we are building PNNL's expertise in analytical chemistry and bioforensics by developing an experimental plan to accept the samples and process them for analysis by several methods will be implemented. We are also developing a protocol for isolating and characterizing LPS from cell mass of BSL-2 vaccine strain of *Y. pestis* cultured at PNNL. The methods for carbohydrate and lipid analysis of LPS will be refined on those samples. The carbohydrate and lipid analysis for marker type and abundance can be coupled to IRMS for compound specific isotope measurements. The desired outcome is to determine potential markers of laboratory culture versus growth in a natural host.



*The left panels show a mixture of bacteria (*E. coli*; small dark rods) and rabbit block cells (bright spheres). The right-hand side panels show the successful separation of the bacterial cells from the blood cells by fluorescence-activated cell sorting.*

A key challenge was to develop methods to recover bacteria from infected animals. During FY 2010, we developed two different methods for separating bacterial cells from animal tissue using blood as a test tissue. One method is based on centrifugation, and the other uses fluorescence-activated cell sorting. Because *Y. pestis* causes serious disease in humans, it must be propagated and harvested in a Biosafety Level 3 (BSL3) facility, which is not available at PNNL. We established a collaboration with the Battelle BSL3 laboratory in West Jefferson, Ohio. In FY 2011, we produced laboratory cultures of avirulent *Y. pestis* under different conditions and analyzed several chemical signatures of their growth conditions, including fatty acid profiles, peptide profiles, and light element and strontium stable isotope ratios. This data constitute the signatures of laboratory-grown organisms to which those of organisms recovered from the natural rat host will be compared.

Over the last two years, the PNNL team refurbished a laboratory to meet BSL2 and animal care standards so that we could infect rats with an avirulent variant of *Y. pestis* that does not cause disease in humans but does in rodents if a sufficient number is introduced into them intravenously. We obtained approval from the Institutional Animal Care and Use Committee for the proposed protocol. In April 2011, we worked with animal care staff at PNNL to infect Norway rats with an avirulent *Y. pestis* strain and harvest tissues. This experiment was the first time our group or the animal care personnel had carried out a BSL2 infection. The work was completed safely. Tissue burdens from these infections was low. In FY 2012, we will repeat the infections on a longer time course or with higher inoculum in order to harvest enough material for analysis.

Enhanced Bioremediation of Uranium Contamination at DOE Sites Via Novel Directed Evolution of Uranium Specific Reductase on Bacteriophage Surface

Hongjun Jin, Philip E. Long, Thomas C. Squier, Michael J. Wilkins, Jianying Shang, Chiann-Tso Lin, Janin A. Khaleel

◆ We propose a multidisciplinary collaboration to study systematically the bacteriophage-bacterial interactions in the uranium subsurface contaminated Rifle Integrated Field Research Challenge (IFRC) and use this information to enhance U(VI) bioremediation. ◆

Contamination of groundwater, soils, and sediments by uranium or other long-lived, soluble radionuclides is a significant environmental problem. Without amendment, these soluble wastes will cause severe environmental consequences because they will eventually disperse into larger areas posing threats to civilian population. Reduction of soluble U(VI) to less soluble U(IV) through environmental microbes is a powerful method for bioremediation of uranium or other radionuclide wastes at contaminated areas. Many toxic metals and radionuclides can be precipitated and immobilized by bacterial-mediated bioreduction brought about through acetate injections into the subsurface. Uranium is not an essential nutrient for bacteria; rather, the biogeochemistry of this soil system is dominated by iron and sulfate reduction, whose presence may potentially limit the rate and extent of uranium reduction. Further, termination of acetate injections may result in increases in oxygen levels and the reoxidation of U(VI).

About 1/40th the size of most bacteria, bacteriophages thrive wherever bacteria grow in ocean, soils, and groundwater. Preliminary ecology studies at Rifle IFRC suggested that groundwater bacteriophages were up to 14-fold higher than bacterial abundance. Several metagenomics studies suggested that bacteriophage genes are widely present in bacterial genomes from groundwater samples at DOE sites. As a result, bacteriophages provide a powerful gene delivery tool for bioremediation applications that overcome current limitations involving acetate-mediated enrichment of anaerobes capable of reducing uranyl. Advantages of bacteriaphage delivery systems include lack of toxicity to human, animals, or plants; scalable synthesis; and targeted self-assembly at sites of contamination.

This research will create highly active specific reductases for U(VI) through directed evolution using phage display technique. When the selected uranium specific reductase gene(s) are delivered into environmental bacterium through bacteriophage vectors, the rate of reduction of U(VI) to U(IV) should be greatly enhanced. This work will create new bioremediation approaches for uranium cleanup with applications to other redox-sensitive metals, both a novel scientific breakthrough and a potential long-term field application. Expected outcomes include a novel prototype technique for cleanup of radioactive waste using bacteriophages that can be deployed at DOE sites. For example, naturally abundant bacteriophages at Rifle IFRC can be isolated and optimal bacteriophage infection and expression of uranyl reductases optimized in environmentally important *Geobacter* sp. (YF-12) to facilitate engineering recombinant phage for uranium field experiments.

In FY 2011, we tested three different metal reductases for uranium reductions. We found the best candidate for further phage display involved UraR from *Gluconacetobacter hansenii* ATCC 23769. We have solved the x-ray crystal structure of UraR and submitted the coordinates from the crystal structure to the PDB database (PDB file: 3S2Y). UraR is a tetrameric protein, with one bound flavin mononucleotide (FMN) per subunit. Proximal to the FMN and present at the interface between adjacent subunits is a cationic pocket that contains a bound chloride that is both suitable for binding the $UO_2(CO_3)_3^{4-}$ anion and at an optimal distance for hydride transfer. These preliminary results suggest a structural basis for the ability of UraR to reduce a broad range of heavy metals (including uranium). Due to the solubility and uranyl reduction property, UraR is a good starting enzyme for rationale design of uranium specific reductase using phage display system aimed at using bacteriophages for enhanced uranium bioremediation.

Also in FY 2011, we successfully established three randomized mutation pool screening for chromate/uranium reduction with T7 bacteriophage bearing polypeptides derived from *Shewanella oneidenesis* (MR-1), *Geobacter sulfurreducens*, and *G. bemidjiensis*. The high throughput screening of enzymatic function for those mutation pools were tested with chromate reduction experiments. Potential chromate reduction phage mutations were tested with multiple rounds of screening and positive mutations were isolated and DNA sequenced. We found that several small peptides derived from these mutation pools showed promising chromate reduction.

We also demonstrated an ability to engineer T7 bacteriophage bearing UraR and a β–amyloid peptide (Aβ2) capable of chromate and uranium reduction. TEM and XAFS found that recombinant T7 bacteriophage exhibiting Aβ2 is able to reduce U(VI) to U(IV) at the phage surface. For FY 2012, we will use a directed evolution approach to optimize UraR for uranium reduction. Engineered bacteriophage will be tested at both laboratory- and column-scale using Rifle IFRC sediments.

Higher-Throughput, More Sensitive Stable Isotope Probing

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

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

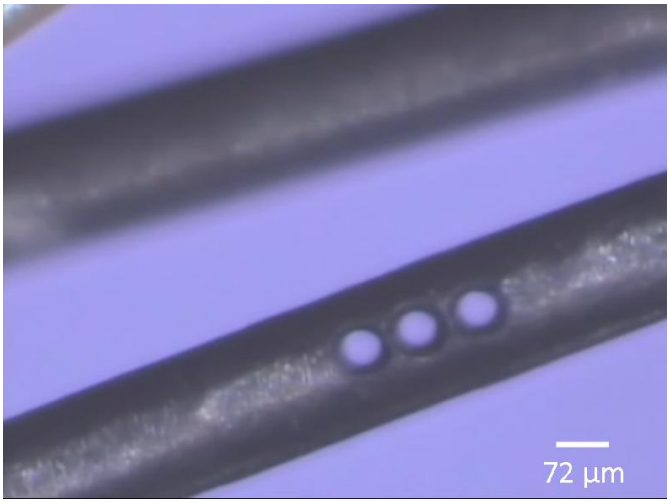
Stable isotope probing, an experimental approach that allows identification of microorganisms within a community that consumes a particular substrate, has been a breakthrough technology that permits a culture-independent association of function with phylogenetic groups. We propose to develop improved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

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

At present, the sensitivity of stable isotope probing is limited by the methodology, which selects stable isotopically labeled nucleic acids by buoyant density centrifugation. In order for a labeled molecule to separate from its unlabeled brethren, it must incorporate a significant percentage (e.g., 20%) of the labeled atoms, which can obscure the detection of early incorporation events in a community. Our approach is to isolate ribosomal (r)RNA from a community exposed to a ^{13}C-labeled substrate of interest, subject it to a sequence (phylogeny)-based separation, and measure the ^{13}C content of sub-populations of the rRNA directly. Direct measurement of the rRNA isotopic content will provide greatly enhanced sensitivity (less than 0.1% enrichment will be detectable), permitting the association of phylogenetic groups of micro-organisms with the earliest events in the breakdown of cellulose and enabling finer time-resolution analysis of the process. Further, our approach should greatly decrease the time required for analysis. Although we have selected cellulose degradation as the experimental process to dissect, the improved technology could be applied to any microbial community and process.

In late 2009 and FY 2010 as one part of this project, we focused on developing new technology for C isotope ratios to decrease sample size requirements, important for the analysis of microbial communities. We developed the most sensitive laser ablation-combustion-isotope ratio mass spectrometry method to be described in the literature, reducing the sample size required for analysis by nearly 1,000-fold (refer to the figure). A paper describing this system was published in *Rapid Communications in Mass Spectrometry*. The system attracted national attention and was highlighted in several media outlets, including *ScienceNOW* and *Wired*.

We also developed a capillary waveguide spectroscopy system and showed that our system could measure isotopic content of 25–30 pmol CO_2, offering the potential for analyzing the C from a few microbial cells. A manuscript describing this system has been submitted for publication to *Reviews of Scientific Instruments*.



Single hair with three holes made by laser ablation. Each hole provided sufficient material for several carbon isotope ratio measurements.

Progress on other specific tasks included:

Moving wire interface. This task began in FY 2010 with major components of the system built. Continued work during FY 2011 saw the interface built in the Instrument Development Laboratory of EMSL. In FY 2012, it will be integrated with the isotope ratio mass spectrometer.

Laser ablation-IRMS. In FYs 2009 and 2010, we successfully constructed and tested laser ablation-combustion-IRMS. Measurement accuracy and precision were similar to standard techniques, and the sample size requirement was reduced nearly 1000-fold. Because of its high precision, the laser ablation sampling method can be used to distinguish metabolic pathways for lightly isotopically labeled carbon compounds and possibly natural abundance samples, making

it superior to other single-cell isotope measurement techniques such as Raman spectroscopy.

Capillary waveguide spectroscopy. We developed a capillary waveguide system to measure isotope ratios of CO_2 with orders-of-magnitude greater sensitivity than has been previously reported. In FY 2010, the system was integrated with the laser ablation unit and combustion reactor, and measurements were made on ablated, combusted solid samples with very promising results.

Oligonucleotide/magnetic bead capture of rRNA. A world leader in sequence-specific RNA capture for isotope ratio measurement, Dr. Barbara MacGregor visited PNNL in summer 2011 and collaborated with our group. We have now successfully captured target RNA populations from mixtures and are working to optimize recovery.

Site-specific RNA cleavage. We are optimizing procedures for cleaving selected RNA molecules using both RNAse H and deoxyribonucleozymes (DNAzymes). We have developed probes for both technologies that appear to provide specific cutting of the desired RNAs. Experiments are underway to test this apparent specificity. If we can selectively cleave target RNAs into smaller fragments, we can separate those smaller fragments from a bulk sample and recover them for isotope ratio measurements using capillary electrophoresis.

Capillary electrophoretic separation and collection of RNA molecules. We have successfully separated RNA molecules of different sizes via capillary electrophoresis, and collected separated molecules in fractions. We are experimenting with different RNA labeling techniques to increase the sensitivity of RNA detection. This technology will be used in combination with RNA cleavage to recover RNA from specific organisms or groups of organisms.

Sample communities for testing improved stable isotope probing methods. We are culturing several bacterial species that can degrade cellulose. Some are obligate aerobes, some are facultative anaerobes, and others are strict anaerobes. We plan to demonstrate our stable isotope probing methods by incubating mixtures of these organisms with ^{13}C-labeled or unlabeled cellulose under aerobic or anaerobic conditions, and show uptake of ^{13}C into RNA of specific members of the mixture.

Identification of Functional Proteins Relevant to Bioenergy and Disease Pathology by Multiplexed Activity-Based Protein Profiling

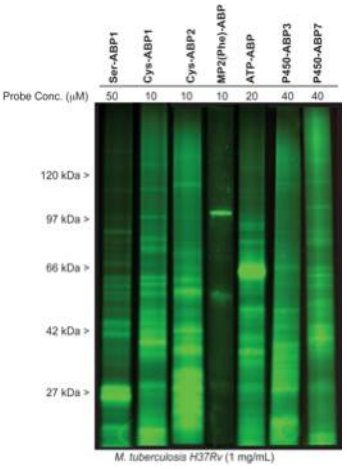
Aaron T. Wright, Jon K. Magnuson, Ellen A. Panisko, Sergey Stolyar

◆ This project is focused on the development of a sensitive and broadly applicable chemical proteomics technology, multiplexed activity-based protein profiling, for the characterization of functional enzyme activities from myriad organisms. The application of this method is facilitating an improved understanding of lung pathogen pathogenesis and biosynthetic energy production. ◆

To isolate, enrich, and characterize functional proteins in complex proteomes, activity-based protein profiling has emerged as a technology in the evolution of post-genomic proteomics. The goal of this capability is to apply chemical probes that directly report on the functional activity of enzymes within the proteomes in which they are naturally expressed. To realize the rapid and sensitive individual measurement of multiple enzymes from unrelated families simultaneously in native samples, we are transforming this technology into a multiplexed, *in situ*, and quantitative approach. The multiplexed activity-based protein profiling (MABPP) technological platform is developed to be an approach that is readily capable of contributing to widely different biological systems. We are applying the technology to provide functional annotation and gain a better understanding of key enzymatic functions in the lung pathogens *Mycobacterium tuberculosis* (*Mtb*) (bacterial) and *Aspergillus fumigatus* (fungal). Additionally, we are demonstrating the utility of this approach in identifying enzymes important to biosynthetic fuel genesis including fungal lignocellulose degradation and microalgal hydrocarbon synthesis.

Our FY 2010 activities focused on integrating organic chemistry and MS-based proteomics to develop multiplexed activity-based protein profiling technology and employ the technology in human health relevant research. We used synthetic organic chemistry to prepare a chemical enzyme probe suite to target the following enzyme families: terpene synthases, cytochrome P450s, serine hydrolases, phosphatases, and glycoside hydrolases. Each probe was developed with a chemical handle, permitting the attachment of either a fluorescent tag or an enrichment moiety to the enzyme-probe covalent complex. Upon probe completion, biological sample labeling was optimized. Concentration studies were also performed to determine optimal enzyme labeling conditions by adding a probe to a sample followed by attachment of a fluorescent group and subsequent gel electrophoresis analysis to identify labeling.

During FY 2011, we were focused on four primary tasks: the completion of the probe suite, with a primary emphasis on developing novel probes for *Mtb* cytochrome P450 enzymes; the application of MABPP to *Mtb* and *A. fumigatus*; the refinement of the cleavable chemistry process requisite for identifying chemical probe labeled peptides; and culturing and preliminary analysis of *Trichoderma reesei* lignocellulose degradation. We completed the synthesis of the full probe suite, with the addition of novel probes targeting phosphatases using a phenolic vinyl sulfone. For *Mtb* P450s, we used the established antifungal drug compound architectures, econazole and ketoconazole, which are known to interact with the enzyme heme core. Though little is known about antifungal-Mtb P450 interactions, it is well documented that several strains of the pathogenic bacteria are susceptible to therapeutic intervention with these drugs. It is presumed that this susceptibility is due to the inhibition of P450 enzymes that are critical for detoxification and steroidogenesis.



Labeling of Mtb *H37Rv.*

Our second focus was on the measurement of *Mtb* and *A. fumigatus* functional enzyme activities using gel-based screening efforts to validate probe reactivity, and mass spectrometry to characterize probe-labeled proteins. An example of gel-based probe labeling is seen in the figure. The diversity of protein band labeling is apparent among different probes, and demonstrates the unique enzyme reactivity of the individual probes. We have worked with our collaborators at Seattle Biomedical Research Institute (SBRI) to identify functional serine and cysteine hydrolases and ATPases including kinases in log-phase grown *Mtb* H37Rv grown in BSL3 conditions. We performed LC-MS measurements on a LTQ Velos Orbitrap MS instrument evaluating both individual probe reactivity and multiplexing of probes to determine if the multiplexed method maintains the profiling coverage of each individual probe. Initial bioinformatic analysis revealed the confident identification of nearly 40 serine hydrolases, 60 cysteine hydrolases, and 100 ATPases. Importantly, nearly 25% of all labeled proteins had no prior function assigned. Additionally, the multiplexed samples fully covered the

enzyme profiles of the individual probe labeling samples. We are currently working to identify the specific probe-labeled residues that will provide further confirmation of the enzymatic functions.

The second phase of our lung pathogen analysis was the identification of kinases, phosphatases, and serine hydrolases in *A. fumigatus*. We chose to culture *A. fumigatus* in nutrient-rich media and media supplemented with human serum. The latter condition was used to identify the fungal response to the presence of human proteins. Though gel-based labeling was not as dramatic as with tuberculosis, we identified several differences in functional activity in response to the human serum, and differences in those responses over time. We submitted nearly 100 MS samples, and their analysis will be completed on a LTQ Velos Orbitrap by the end of the current year.

Our third emphasis was on an aspect of our proposal that has proven incredibly difficult. This goal is the selective identification of probe-labeled peptides. Our desire is to annotate the specific amino acid residues reacting with our probes. This is a complex task that requires enrichment of probe-labeled proteins on streptavidin agarose, followed by on-bead trypsin digestion, and then chemical treatment to break a chemical bond that we insert between the enrichment moiety and our chemical probe-labeled peptide. This cleavable chemical bond facilitates the selective release of probe-labeled peptides for MS analysis. We screened through a number of cleavable moieties including photolabile elements, acid cleavable aromatic moieties, a sodium thiosulfite labile linker, and a tobacco etch virus peptide cleavage site to no avail. This year, we collaborated with the California Institute of Technology, with which we worked to incorporate a polyoxysilane cleavable moiety that resists cleavage under copper promoted “click-chemistry” conditions requisite for MABPP, and by strong detergents and denaturants, but cleaves remarkably well with high reproducibility with just 5% formic acid in water.

In FY 2012, we will finish the MS analysis of a number of these probe-labeled peptides from all biological aspects of this project. We will also focus on the identification of probe-labeled peptides using our cleavable approach for both health and energy relevant research. With regard to bioenergy production, we will do LC-MS based analysis of secreted enzymes from multiple strains of the lignocellulose degrading fungi, *Trichoderma reesei*, and will characterize hydrocarbon biosynthetic enzymes in *B. braunii*.

Integrated Nano-Scale Imaging for Investigating Applications and Implications of Nanomaterials

Galya Orr, Dehong Hu, Alice Dohnalkova, Derek F. Hopkins, Jay W. Grate, Ponnusamy Nachimuthu, Ajay S. Karakoti, Shail P. Sanghavi, Ping Yang, Sindhu Thevuthasan

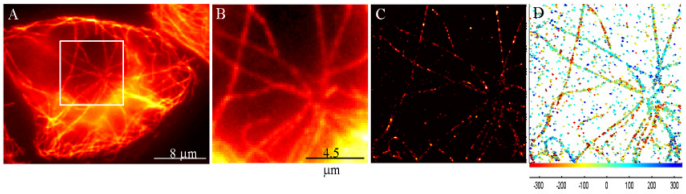
◆ We aim to develop new integrated chemical and structural imaging approaches that will support the investigation of nanomaterial interactions with biological systems and polymers to enable and accelerate their safe applications in nanotechnology. ◆

The unique properties of materials at the nanoscale have been explored for multiple industrial and medical applications. These applications are expected to increase both unintended environmental or occupational exposures and intended medical or direct consumer exposures. However, the impact of such exposures on human health is unclear, and therefore the applications of nanomaterials are currently held back. Accumulating observations demonstrate the potential of engineered nanomaterials to impose adverse effects on living systems, but a great deal of confusion still exists about the properties that make a particle toxic or biocompatible. It thus becomes critical to evaluate toxicity or biocompatibility under low dose and realistic exposure conditions and to study the underlying mechanisms by investigating individual nanoparticles or nanoscale aggregates.

To meet the above challenge, this project first provides three-dimensional high-resolution fluorescence imaging integrated with x-ray imaging and tomography for investigating cellular processes with nanometer resolution in the intact cell. This approach will provide a molecular-level insight into the spatial distribution of specific proteins, molecular complexes and organelles, as well as individual nanoparticles within the cellular environment, leading to new understanding of their behavior and function in cell response and survival. Second, this project integrates chemical spectroscopy and imaging approaches that will provide a better understanding of the distribution of individual quantum dots in the polymer matrix. This will enable their use in solar energy applications with a focus on studying the photo-induced variations in the electronic structure and the energy level alignments that determine exciton formation, charge separation and transport that essentially control the efficiency of the hybrid solar cells.

Nanomaterials in the living cell. In FY 2011, we commenced developing new imaging approaches to investigate individual nanoparticles and their interactions with living cells, providing the data needed to accelerate safe applications of nanotechnologies. The potential toxicity or biocompatibility of nanoparticles is governed by the cellular interactions and fate of the particles, which dictate the cellular response and ultimately determine the impact on human health, but the relationships between particle properties and these cellular processes are far from being understood. Investigations of these relationships have been challenged by the limitations of current research technologies and by the strong tendency of nanomaterials to agglomerate under experimental conditions. Agglomeration leads to larger particles, providing information that is irrelevant to nanoscale materials and the exposure in vivo. We have been focused on developing new approaches that will allow us to study individual nanoparticles within the intact cellular environment, one nanoparticle at a time, to delineate particle properties and cellular processes that are relevant to the individual nanoparticle and the exposure in vivo. By taking advantage of our experience in single-molecule fluorescence techniques and working with the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, we have been developing approaches to obtain three-dimensional chemical and structural images of individual nanoparticles within organelles in the intact cell with nanometer resolution. These approaches have been applied to investigate the cellular interactions and fate of individual nanoparticles to identify nanoparticle properties that are toxic or biocompatible and delineate the underlying mechanisms.

Building on our experience in single-molecule fluorescence imaging, we developed stochastic optical reconstruction microscopy (STORM) in three dimensions by introducing a cylindrical lens in the emission pathway, which slightly distorts the image of single-molecules according to the axial location of the molecule relative to the focal plane. The distorted images have been translated to distance from the focal plane based on the pixel number and intensity along the x and y axes. The translation and the reconstruction of the three-dimensional STORM images have been accomplished using the algorithm we developed within our current two-dimensional STORM software. Using this approach, we acquired three-dimensional images of microtubules in the intact hydrated cell with 20 to 30 nm resolution. We expressed fluorescent clathrin, caveolin, or actin in alveolar epithelial cells and exposed the cells to nanoparticles that were tagged with the photo-switching dye, Alexa 647. Clathrin, caveoli, and actin were expressed as fluorescent chimeras with the photo-switching fluorescent protein, FastLime, enabling both the proteins and the particles to be imaged using STORM.



A. Conventional fluorescence image of microtubules in the intact alveolar epithelial cell. B. Enlarged conventional fluorescence image of the area marked by the square in A. C. Super resolution fluorescence image of the area in B. D. Three-dimensional representation of the image in D. The scale shows the distance (in nm) from the focal point (0) in the Z axis.

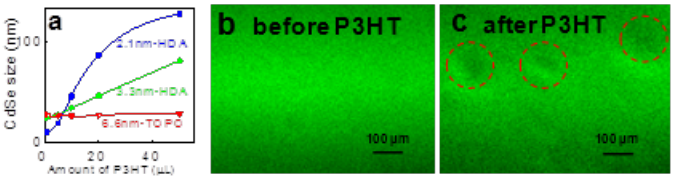
Using red laser (660 nm) to excite the particles, and green laser (473 nm) to excite the proteins, we acquired images of cellular structures and nanoparticles in the intact cell with 20 to 30 nm resolution. We wrote a successful user proposal that granted us time on two of the most competitive beam lines at ALS, enabling the use of the scanning transmission x-ray microscope (STXM) for imaging and tomography with 20 nm resolution. In collaboration with ALS scientists, we have been developing the approaches to investigate individual nanoparticles in the intact alveolar cell to gain information about the chemical state of the particle inside organelles. These methods will provide an unprecedented understanding of the complex and reciprocal relationships between the nanoparticle and the cellular environment.

CdSe quantum dots. In semiconductor quantum dots-polymer hybrid solar cells, the chemical interaction between the quantum dots and the polymer matrix is one of the key elements in achieving high power conversion efficiency. A fundamental understanding of the photoinduced interaction between CdSe quantum dots and the poly (3-hexylthiophene) (P3HT) conductive polymer matrix will immeasurably assist efforts to design optimum thin film structures for efficient solar cells. Although semiconductor quantum dots-polymer hybrid solar cell system has been studied extensively for solar cell applications there exists little understanding of the way in which the quantum dots interact with the polymer matrix. Therefore, we adopted a systematic approach to study the concentration and size-dependent distribution of the CdSe quantum dots in P3HT and understand how these variations influence the photoinduced charge transfer. This includes characterization of geometrical, chemical, and electronic structure interaction between CdSe quantum dots (varying size between 2 and 5 nm) and polymers at the molecular level by applying existing and newly developed tools. Results from this study provide critical insight into the fundamental aspects of the energy level alignments that govern charge-transfer dynamics from the quantum dots to P3HT polymer but are unavailable from current examination of hybrid solar cells. The characterization of the films will involve different degrees of spatial and energy resolution involving helium ion microscopy with sub-nanometer spatial resolution, synchrotron-based scanning transmission x-ray microscopy (~20 nm), Resonant inelastic x-ray scattering (RIXS), x-ray absorption spectroscopy and x-ray photoelectron spectroscopy (XPS; ~1 µm), ultraviolet photoelectron spectroscopy (UPS), and cryo-transmission electron microscopy to investigate the concentration and size/shape-dependent distribution of CdSe quantum dots in P3HT polymer films.

During FY 2011, we studied the structure-property relationship and the effect of environment on the electronic and crystalline properties of CdSe quantum dots. The in-situ micro diffraction data show that the CdSe quantum dots capped with trioctyl phosphine oxide or hexadecylamine in toluene exhibit predominantly wurtzite crystal structure, which undergoes a phase transformation to zinc blende crystal structure following drop casting on Si. Further, decreasing the CdSe quantum dots size enhances this phase transformation.

The XPS shows a systematic increase in the core level binding energies of Cd 3d and Se 3d and the band gap with decrease in size. In addition the Cd/Se ratio increases as the size of the quantum dots decreases from 6.6 nm to 2.1 nm, thereby increasing Se vacancies that cause the phase transformation. However, drop-casting CdSe quantum dots on Si alter the arrangement of capping ligands and facilitate significant phase transformation. In addition, we found spectroscopic evidences of charge transfer between P3HT and CdSe quantum dots by photoluminescence spectroscopy (PL). Incorporation of CdSe quantum dots in P3HT results in quenching of the main PL emission from both CdSe and P3HT, and a new emission peak is observed from the recombination of electrons in CdSe with holes in P3HT as shown in energy level diagram. However, incorporation of quantum dots in P3HT matrix at concentrations in which spectroscopic changes are observed, leads to severe agglomeration of quantum dots. To achieve charge separation at the interface, the size and distribution of quantum dots needs to be controlled around the exciton diffusion length of about 10 nm, emphasizing the need to find alternative ways to create a homogenous distribution of quantum dots in the P3HT polymer matrix.

For FY 2012, we will work toward achieving x-ray tomography of nanomaterials with alveolar epithelial cells and begin developing an integrated approach for fluorescence imaging and x-ray tomography. In addition, we will achieve comprehensive characterization of polymer films using He ion microscopy, STXM, imaging XPS, and UPS.



Agglomeration of quantum dots in P3HT observed by a) DLS and soft x-ray imaging b) before and c) after mixing with P3HT.

Massively Parallel Sequencing Technology for the Forensic Identification of the "Unknown" Biological Threat Agent(s) Recovered from the Biological Crime Scene

Rachel A. Bartholomew, Lee Ann McCue, Hugh D. Mitchell, Bobbie-Jo M. Webb-Robertson, Mitch Rawlings, Nathan A. Baker, H. Steven Wiley, L. Meng Markillie, Timothy M. Straub

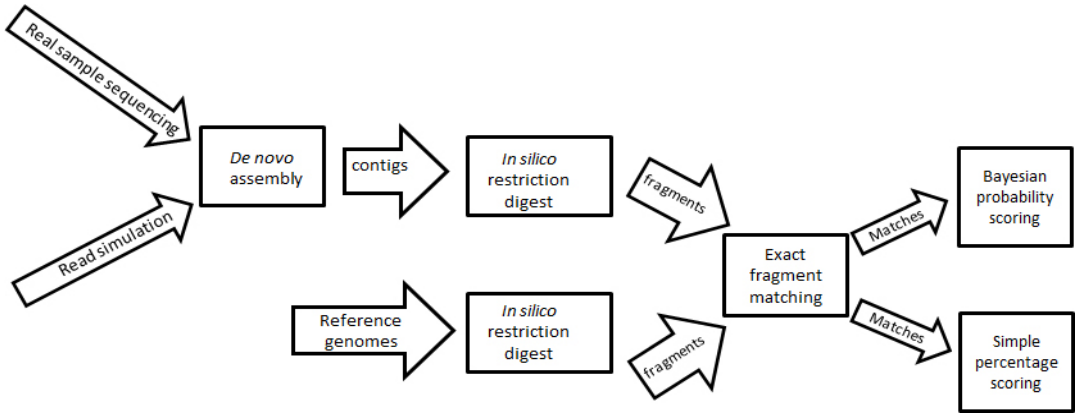
◆ A major challenge to law enforcement and/or the first responder community is correctly identifying the unknown agent at a biological crime scene. One means of identification is through use of massively parallel DNA sequencing (MPS). The aim of our study is to develop and test computational tools for analysis of DNA sequencing data, with the particular goal of identifying an unknown(s) in a biocrime sample. ◆

Many current nucleic acid assays and immunoassays for agent identification are limited by the requirement of basic knowledge of the unknown in order to identify or confirm identification of the sample. We propose to address this problem by developing and testing computational tools to demonstrate proof of principle agent identification of laboratory samples using an MPS-based approach that requires no such knowledge and would provide an alternative and potentially more specific means of identification of an unknown(s). The computational tools will provide innovative means for the identification of an unknown agent, where the test can be conducted without specific a priori knowledge of the target. The aim for these new tools is to focus on providing statistical probabilities of an organism of interest being present rather than determining the complete sequence of that organism.

To accomplish the above goal, we developed bioinformatic tools in FY 2011 that will identify microorganisms with high sensitivity and specificity using only MPS data. Our general approach is to take the short MPS reads from a sample of an unknown organism, assemble these reads into contigs, and perform an *in silico* restriction digest to produce a set of sequence fragments. The ends of the contigs are not bound by restriction sites and are therefore not included in the fragment set. Identification is accomplished by matching fragments from the sample restriction fragments for a reference set of the complete genomes of microorganisms of interest.

We are using publicly available open source tools to assemble the MPS reads into contigs. We have tested Ray, which works as-is for Illumina and Roche MPS data, but does not properly assemble color space data from Applied Biosystems. For this reason, we switched to ABySS, which is also publicly available and can assemble color space data. Continued research into available assembly programs may be useful, as our goal is to develop a species identification method that can be used regardless of the MPS platform used to generate the data. Similar *in silico* restriction fragment sets were generated for the assembled contigs of our "unknown" sample and the reference genomes of organisms of interest (using genomic data available in the public domain). Closely related organisms were included to examine the sensitivity and specificity of the method. We then applied classification methods to compare the "unknown" fragment set to the reference sets. Our goal is to determine probability of the species (e.g., identification), given a set of references and short read fragments.

Publicly available MPS data from *Bacillus anthracis*, *B. cereus*, and *B. subtilis* were utilized for the initial proof of principle demonstration of our general approach. These data were appropriate for initial development and testing; however, one of the challenges of using data only from the public domain is that the available MPS data did not necessarily have an exact match (species and strain) with an available complete genome. Only in the case of *B. subtilis* did we have matching MPS and complete genome data for *B. subtilis* ssp. *subtilis* str. 168. Analysis of the *B. subtilis* 168 MPS data (Illumina) resulted in high percentage matching (0.81) to the



Analysis flowgram for massively parallel sequencing data.

B. subtilis 168 genome and a much lower percentage (<0.04) for any other *Bacillus* or *Yersinia* genome. Analysis of the *B. anthracis* MPS data resulted in roughly equal probability matches to the several *B. anthracis* strains with available complete genomes. Similar results were obtained with *B. cereus*.

To test our ability to discriminate between similar genomes even when sample data is not available, we used *dwgsim* in the freely available *dnaa* software package to generate simulated MPS data. This program produces simulated reads from a specified genome, allowing us to test our ability to assemble and match these reads back to the correct genome. We generated reads for *Francisella tularensis holarctica* LVS (pathogenic), and *F. novicida* U112 (similar sequence but non-pathogenic). Our method correctly identified the pathogenic strain (>99.995%) and the U112 (100%). These results show that our approach can consistently discriminate between high and low pathogenic genomes, even when these genomes have highly similar sequences. Recent efforts have focused on developing a scoring technique based on Bayesian probability, thus providing a probability for each genome's match to a sample rather than a simple matching percentage.

In FY 2012, we will generate MPS data using the SOLiD platform to test these tools using real laboratory samples (single organism and mixed samples), to determine the sensitivity and specificity of both MPS and the newly developed analytical tools on MPS sequencing data generated at PNNL. As part of the LDRD effort in FY 2011, we established a collaboration team with Northern Arizona University (NAU) led by Paul Keim, a world-renowned *Bacillus anthracis* researcher. NAU will provide the DNA to demonstrate proof of principal testing of the PNNL-developed analytical tools.

Microbial Processes Accompanying Deep Geologic CO_2 Sequestration

Michael J. Wilkins

◆ This project aims to increase understanding of the impact of geologic CO_2 sequestration on microbial biomass and viability. Deep subsurface locations for CO_2 storage contain microbial populations that may impact gas generation, caprock integrity, and other parameters that need to be better understood when planning and modeling the behavior of these sites. ◆

The capture and storage of carbon dioxide in deep geologic formations represents one of the most promising options for mitigating impacts of greenhouse gases on global warming, owing to the potentially large capacity of the formations and their broad regional availability. CO_2 is injected into formation fluids, nominally saline aquifers, as a supercritical fluid ($scCO_2$) at depths >2500 m that maintain its supercritical state. Studies on "deep biosphere" have demonstrated that microbial communities are present in all environments that have been suggested as suitable locations for geologic carbon dioxide sequestration. In some industries, $scCO_2$ is used as a sterilizing agent; however, field trials have detected microbial activity after CO_2 injection, suggesting that indigenous bacterial strains are able to tolerate these extreme conditions. The persistence of bacteria in these environments is important, because these microorganisms may affect long-term storage of CO_2 in a number of ways. Bacteria may act as reaction sites for increased rates of mineral precipitation, generate mineral precipitates as a result of their metabolism, and may also generate methane gas within the storage location.

There is a critical need for a rapid, high-sensitivity, high-resolution technology to profile the functional activity of multiple enzyme families in a single experiment. This project will describe the development of multiplexed activity-based protein profiling, a novel high-resolution and high-sensitivity mass spectrometry platform to characterize functional enzymes from multiple enzyme families in their native proteomes in a single experiment. Multiplexed activity-based protein profiling is required for characterizing novel functional enzymes, low abundance functional enzymes, and functional enzyme differences between unique proteome types/states, and for facilitating genome annotation of previously uncharacterized organisms. Additionally, multiplexed activity-based protein profiling will identify proteins quantitatively using single peptide identification.

Specifically, we will initially apply the protein profiling to diverse biological proteomes for identifying and characterizing functional enzymes critical to disease pathogenesis and bioenergy. Functional enzyme families will be characterized that may contribute to tuberculosis and aspergillosis infection, including cytochrome P450s, glycoside hydrolases, and acid phosphatases. Novel glycoside hydrolases and carbohydrate esterases will be identified in extremophile fungi that degrade lignocellulose; improved variants of these enzymes are key to the use of non-food feedstocks for economical biofuel generation. For multiplexed activity-based protein profiling, we will characterize terpene synthase family enzymes in *Botryococcus braunii* that generate long-chain branched alkene hydrocarbon oils, which could be used directly as infrastructure compatible biofuels. In short, this work will demonstrate the capabilities of multiplexed activity-based protein profiling and reveal its utility across multiple research fields.

To date, we initiated metabolic studies of a model deep subsurface bacterial species using novel tools developed at PNNL. Using high-pressure nuclear magnetic resonance (NMR) analysis, we have been able to track the growth of these bacterial strains under high pressure and temperature conditions, and track the consumption of a carbon source. We demonstrated consumption of a ^{13}C-labeled carbon source at ~5 MPa and 37°C. When the reaction vessel pressure was increased to ~10 MPa, carbon degradation ceased, suggesting that the biomass was killed under these conditions. Further use of this technique will allow us to determine the limits up to which growth and respiration will occur. In addition, we have constructed a high-pressure incubation reactor that can simulate supercritical conditions. This will allow bacterial cultures to be exposed to deep subsurface conditions before further physiological and metabolic analysis. The reactor also incorporates a high-pressure pH probe that will enable us to track the effects of $scCO_2$ on groundwater/media pH. Finally, deep subsurface groundwater samples have been obtained from an injection test-site in Wallula, WA. These samples have been incubated under anaerobic conditions with organic contaminants frequently co-injected with CO_2 (e.g., ethanolamine) to try and enrich for strains that may be able to utilize these compounds for growth and respiration. Once such strains are isolated, they will be used in further laboratory-based studies.

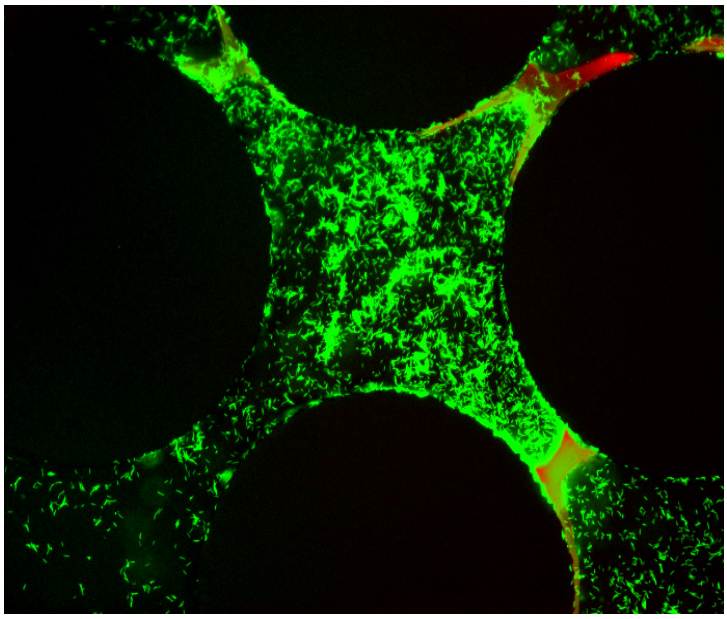
During FY 2012, our plans involve the operation of a high-pressure batch apparatus for enriching microbial populations in the presence of organic material. We will test the effects of $scCO_2$ on microbial processes within this apparatus, and the effects will be monitored by tracking sulfate-reduction rates following different exposures to $scCO_2$. Using high-pressure NMR tracking, we will monitor both the metabolic status of sulfate-reducing populations and the effects of biomass (whole cells, peptides, proteins) on mineral carbonation reactions under $scCO_2$ conditions.

Micro-Fluidic Models for Studying Microbial Communities—Integration of Micro-Fluidic Model Experimentation, Multimodal Imaging, and Modeling

Michael J. Wilkins, Jay W. Grate, Changyong Zhang, Haluk Resat, Galya Orr, Vanessa L. Bailey

◆ This project utilizes novel microfluidic platforms coupled to multi-modal imaging technologies to investigate microbial cellulose degradation at the pore scale. A better understanding of soil carbon flux is key for the development of modeling tools for predicting carbon cycling in the environment, with implications for both climate change and land use policy. ◆

Cellulose is both the primary structural component of plants and the most common organic compound on Earth. The global carbon cycle is an interplay between carbon reservoirs in the atmosphere, oceans, subsurface, plants, and soil, with microbial communities mediating many of the transformations between reservoirs. The flux of microbially-generated CO_2 from the soil to the atmosphere remains the least constrained component of the terrestrial carbon cycle. At 75–100 billion metric tons of carbon per year, it is the second-largest terrestrial C flux and an order of magnitude larger than anthropogenic fossil fuel combustion. Approximately 10% of atmospheric CO_2 cycles through the soil annually, and yet the temporal and spatial dynamics of soil respiration remain difficult to model or predict.



A well-characterized cellulose-degrading species Flavobacterium johnsoniae *cells colonize pore spaces within the microfluidic habitat. The highest densities of cells are associated with the "islands" of deposited cellulose.*

Within subsurface environments, cellulose degradation occurs within pore spaces where a range of advective and diffusive biogeochemical processes produces local microenvironments. These different environmental conditions can affect both the distribution of microbial communities within the subsurface and subsequent rates of cellulose degradation. Microfluidic models are small flow cells consisting of a series of vertical columns that act as grains, resulting in specific pore sizes and pore throats. Therefore, these microfluidic models are effective proxies for subsurface environments. In addition, they are engineered to enable the application of multiple imaging-based technologies to interrogate processes occurring at this pore scale in a non-destructive manner. Understanding these pore-scale microbial processes affecting rates of cellulose degradation in the subsurface is fundamental to our ability to predict and model aspects of global carbon cycle.

Using the aforementioned novel platforms that can be configured to imitate soil pore spaces, this project studies controls on rates of microbial cellulose degradation across spatial scales and chemical gradients. Data obtained from these experiments can then be used to refine modeling approaches for terrestrial C cycling. We will integrate the technologies arising from a number of other projects. Microcrystalline cellulose will be deposited within microfluidic models, and the subsequent microbial degradation imaged using novel fluorescence-based techniques. In addition, oxygen abundance and the development of microaerophilic zones within the pore structure will be imaged using novel oxygen-sensor probes. This imaging of microbial cells within the microfluidic model will incorporate the advances made by a project that aims to use the Raman detection of ^{13}C incorporation in single cells grown on cellulose and of species-specific signatures in single cells. Our general efforts in this project are aimed at developing the following:

- micro-fluidic models for studying the transformation of insoluble polymeric carbon by microbial communities
- multimodal nondestructive imaging of consumption of substrates and production of cells

- micro-fluidic models, multimodal imaging, and individual-based modeling of microbial community processes to improve mechanistic understanding of how complex environmental systems behave
- an improved understanding of how differences in habitat diversity and the spatial coupling of electron acceptor and (initially) insoluble electron donor affects rates of cellulose degradation and microbial community composition.

In FY 2010, our work focused on micromodel design for subsequent experiments. A range of micromodel designs that vary in relative advection and diffusion processes have been modeled, demonstrating the ability to generate zones of variable flux and diffusion within the models. During FY 2011, significant progress has been made in developing these experimental platforms:

- Micromodels with a range of different pore structures have been manufactured using the oxygen-permeable polymer PDMS.
- Cellulose nanocrystals have been synthesized using a novel HBr digestion technique of Whatman filter paper. These nanocrystals can be utilized by cellulose-degrading bacteria, and are amenable to introduction into microfluidic platforms.
- These cellulose nanocrystals have subsequently been "tagged" with a fluorescent marker (an Alexa dye) that enables visualization of this carbon compound using epifluorescence microscopy
- Further developing a point above, cellulose "resource islands" have been generated within PDMS microfluidic platforms by flowing alcohol-based suspensions of cellulose nanocrystals into the pore spaces. Subsequent heating and evaporation of the alcohol allows the deposition of cellulose.
- Cellulose-degrading bacteria (a *Flavobacterium johnsoniae* strain) have been inoculated into these microfluidic structures. The *F. johnsoniae* strain expresses a fluorescent protein that also allows visualization using epifluorescence microscopy.
- These microbial incubations have allowed the colonization of cellulose "resource islands" to be monitored (see the above figure).
- In a parallel series of batch experiments, a range of cellulose-degrading bacterial species have been incubated together in the presence of cellulose nanocrystals to calculate batch kinetic parameters associated with cellulose degradation (cell growth rate, cellulose degradation rate). These parameters can be used in modeling approaches to studying cellulose degradation, and the eventual aim is to compare these batch parameters against measurements taken at the pore scale in the microfluidic platform.

These initial achievements will allow the further development of the microfluidic platform experimentation. In the near-term, we aim to couple observations of biomass growth to depletion of cellulose within the pore spaces (either as surface area changes, or decreases in fluorescence intensity associated with loss of the fluorescent tag). Subsequent work will incorporate oxygen-sensing probes in the microfluidic structure (as either thin films or microparticles), so that the impact of micron-scale oxygen gradients on the rates of cellulose degradation can be assessed. Future work will use a simple constructed microbial community consisting of approximately three different bacterial strains in the microfluidic models, to better represent community structures in the environment. Additional higher resolution imaging of labeled cellulose nanocrystals will allow more accurate cellulose degradation rates to be inferred. Data generated from this project will be directly incorporated into pore-scale modeling approaches for better predicting these processes in the environment.

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

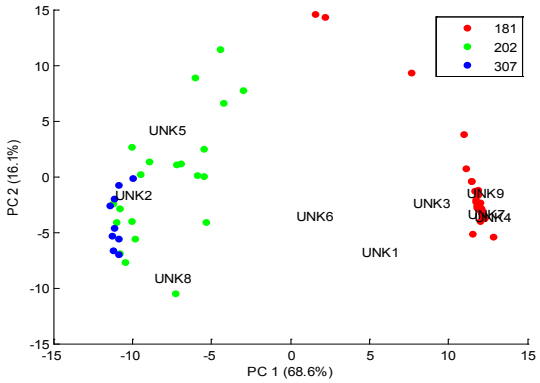
Vanessa L. Bailey, Nancy J. Hess

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

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

Initially, we used surface-enhanced Raman spectroscopy (SERS) to develop spectra for single, live *Escherichia coli* (DH5α) suspended in minimal media with silver nanoparticles. The Raman signature we observed was consistent with data in the literature for aromatic amino acids and nucleic acid bases previously observed for *E. coli*, including the identification of tryptophan, guanine, and adenine. The Raman signature appeared to change as a function of time of exposure to silver nanoparticles. We also collected data for other microbial species (*Xylanimonas cellulosilytica* and *Streptomyces griseus*) grown on the same media in order to discern whether the different species can be differentiated by Raman spectroscopy. All species were grown using both ^{12}C- and ^{13}C-glucose to detect signatures of carbon uptake.

We have since migrated to direct Raman spectroscopy (i.e., not SERS), optimized spectral acquisition parameters and applied signature processing algorithms to enhance sensitivity. We used a suite of uncharacterized microbial isolates, obtained through the University of Wisconsin Cameron lab from leaf cutter ant dump sites. These isolates (di181, di202, and di307) exhibited different growth rates and habits, with di202 pleomorphic, having both a vegetative and spore state.



Principal components analysis: two-dimensional locations of each of the unknown isolates plotted, with the known library of isolates di181, di202, and di307.

Raman spectroscopy and subsequent statistical analysis of spectra distinguished the different microbial species and forms. A principal component analysis (PCA) of the 61 samples showed a clear discrimination of the di181 isolates from the di202 and di307 isolates. Partial Least Squares Discriminant Analysis (PLS-DA) separated all three groups, correctly placing the sporulated and vegetative spectra for di202 within a single class, with a classification accuracy of 96.3% with a standard deviation of only 3.0%. To challenge the classification, we collected Raman spectra from a fresh set of these isolates with no identifying information. Working blind, the PLS-DA classification was able to identify correctly 8 of the 9 unknowns presented. We are confident that further refinement of our statistical tool will continue to improve our classification success.

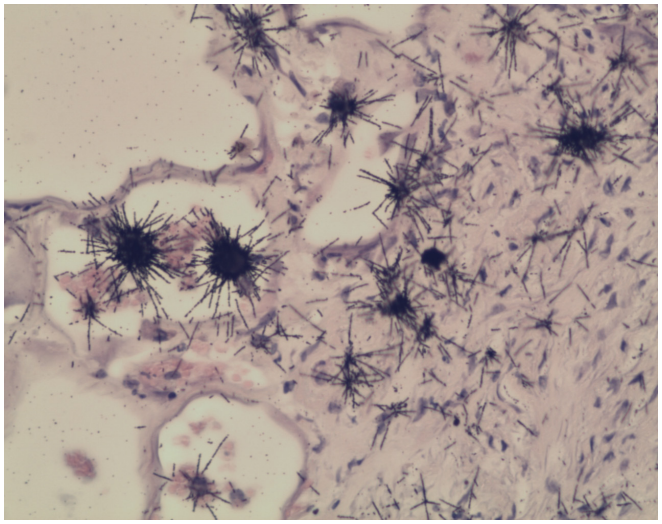
In FY 2012, we will continue data analyses. A primary goal waits on other projects; meanwhile, we will use Raman spectroscopy to non-destructively examine microbial species colonizing a microfluidic chip. We anticipate that Raman spectroscopy will be able to identify the particular species colonizing target niches within the microfluidic platform and also determine which (if any) particular species dominate the colonization of the different niches.

Mining the Data from Research on Dogs Exposed to Internally-deposited Radionuclides

William F. Morgan

◆ In light of concerns about human exposure during radiation-contaminated area cleanup (e.g., the Hanford Site and Fukushima), increasing use of radiation in medicine and industry, and the potential for dirty bombs and nuclear terrorism, we are analyzing these studies to understand potential health effects from radiation exposure in a large animal model system. ◆

Life span studies of beagle dogs commenced in the early 1950s to examine the effect of internally deposited radionuclides on a large animal. These studies were funded by the U.S. Atomic Energy Commission and later by DOE. With a cost in excess of $200 million, the experiments involved over 8000 dogs and lasted until 1993. The beagle was chosen because it has several positive characteristics, including an easy-going demeanor, optimum size, appropriate life span (~14 year mean), and physiological and anatomical similarities to humans. This breed also naturally exhibits similar cancers at the same frequency as humans. The data collected represents a unique resource.



An autoradiograph of a paraffin embedded section of lung tissue from a beagle dog that had inhaled plutonium. The plutonium deposits in the lung and the autoradiograph illustrates the amount of plutonium deposited and the alpha tracks emitted from the deposited plutonium are clearly visible.

The Fukushima accident in Japan highlighted the need to examine potential effects in the most radiation-sensitive human populations, specifically in fetuses and young children. Although we will not study Fukushima, we propose to examine the potential radiation effects in the dogs exposed during pregnancy and in pups at different ages. The connection is that following the Chernobyl disaster, there were approximately 200,000 pregnancy terminations due to fetal radiation effect concerns. The fetuses, infants, and children constitute subgroups of the population at greater risk for detrimental health effects of exposure to ionizing radiation, likely because of their increased radiosensitivity and/or because they have more time to develop disease.

In FY 2010, we determined the feasibility of mining various data types for information on the effects of total dose, dose rate, route of incorporation, and specific isotope. The goal was to interrogate these data using new technologies in molecular biology available at PNNL and subsequently apply modern statistical methodologies for analysis. To this end, we completed the analysis of dogs exposed to ^{137}Cesium at Argonne National Laboratory and the Inhalation Toxicology Research Institute. The investigation involved determining the route of exposure (inhaled or ingested), dose, dose-rate, life span, and primary cause of death.

We completed the pedigree analysis of irradiated dogs in FY 2011 to investigate potential genetic susceptibility to radiation health effects. Initially, we identified the primary cause of death and then determined whether there was a genetic component to radiation-induced disease. With the aid of PNNL investigators utilizing programs that analyze high throughput proteomic data, we devised protocols for determining pedigree analysis and are currently studying potential genetic susceptibility in the dog population. Dr. Dulaney Wilson and Ms. Andrea Brigantic worked on this project, and the results have been accepted for publication in *Radiation Research*.

For upcoming work, we will analyze data from a 25-year life span study of 1330 beagle dogs exposed to a single acute dose of ^{60}Cobalt gamma radiation and sham irradiated controls. Dogs were exposed to 160 or 830 mGy of radiation at three stages *in utero:* at 8 (pre-implantation), 28 (embryonic), or 55 (fetal) days post-coitus two days post-partum (infants), while beagles irradiated at 70 days (juveniles) or 365 days (young adults) post-partum were exposed to a single dose of 830 mGy. Time to death from all causes using survival analysis methods and the six most frequent causes of death using proportionate mortality ratios will be analyzed. We will prepare the results of this analysis for publication.

Next Generation Software for Automated Structural Identification of Metabolites

Lars J. Kangas, Thomas O. Metz, Giorgis I. Mezengie, Bojana Ginovska-Pangovska, Brian T. Schrom; John H. Miller (Washington State University)

◆ This project will reduce the time and cost of biomarker discovery by developing a software product to enable the high throughput and accurate identification of metabolites and other small molecules. Successful development of the software will facilitate studies of fundamental biology and the discovery of disease biomarkers. ◆

Currently, the structural identification of unknown metabolites detected in liquid chromatography-mass spectrometry studies is based on manual interpretation of their tandem mass spectra, which is laborious and typically does not yield a complete identification. The inability to identify endogenous metabolites and other small molecules rapidly and globally has significantly limited the discovery of novel biomarkers of disease and drug toxicity in metabolomics studies. An algorithm that models the fragmentation pathways of molecules in mass spectrometry and generates in silico ion spectra for putative metabolites is required. With a large database of these spectra, unknown metabolites can be identified by comparing the observed spectra against the database.

The software product we propose is anticipated to be of substantial value to laboratories in the medical diagnostic, biotechnology, and pharmaceutical industries, as it will reduce the time and cost of elucidating mechanisms of disease pathogenesis and drug toxicity. In addition, the tool would be indispensible for biofuels research laboratories, as the high-throughput structural elucidation of metabolites could greatly facilitate bioengineering experiments that have as their goal the creation of microbiota that are more efficient in producing hydrogen or ethanol.

In FY 2010, we showed that identifying metabolites accurately, rapidly, and automatically is possible using a software algorithm. An early working version of the algorithm was completed, tested, and trained using spectra from 22 lipid species (metabolites). A set of 45 test lipids were purchased, analyzed, and identified using the algorithm in conjunction with LIPID MAPS, a database with over 22,000 lipid structures provided by a consortium of lipidomics core laboratories. Of the 45 test lipids, 39 were positively identified, and 5 were deemed second most likely identifications. The last lipid only made it to the middle of a short list of possible identifications.

During FY 2011, 25 unique chemical reaction templates were developed that support the algorithm with how bonds and atoms should rearrange when bonds are cleaved in the modeled mass spectrometer. Programming code was developed, tested, and put into the algorithm that makes use of these reaction templates. Modeling the correct chemical reactions will enable us to remove a molecule fragment charge model, developed to temporarily remove false positives lipid identifications that were experienced due to the algorithm not knowing which fragments were neutral and which were charged. The real experimental lipid data analyzed included both the spectrometer data that the algorithm uses and data from liquid chromatography. Models were developed to predict lipid elution times in reverse phase chromatography to increase the belief in the correct lipid identifications.

The algorithm needs two major functionalities for the next year. First, the prediction of fragment charges will be developed from the chemical reactions developed in FY 2011. Second, the more difficult problem is to have the algorithm accept different adduct ions. To date, the algorithm has only searched for hydrogen adducts and for a few specific lipids and ammonium adducts. The algorithm needs more generally to search for all possible adduct ions for every lipid.

There are multiple goals and challenges for this project in FY 2012. We aim to develop a method to calculate charge locations in molecules. The temporary installed method gives fragment charge, not location. The software algorithm generates *in silico* spectra; knowing charge locations will allow it to generate more accurate spectra, which will enable more accurate metabolite identifications. We will also develop a method to search for all possible adduct ions, in both positive and negative mass spectrometry. Some metabolites are observed together with an additional small molecule, an adduct, in a mass spectrometer. These adducts have to be accounted for if possible when analyzing spectra. Lastly, we will test algorithms with other metabolites than lipids. The development has used lipids to date as a well-understood set of molecules, although the intention for the algorithm is metabolites generally. The algorithm will be tested with several know metabolites at hand.

Proteomics Measurements of Functional Redundancy and Stability Testing of Cellulose Degrading Anaerobic Microbial Communities Within Engineered Bioreactors

Stephen J. Callister, Aaron T. Wright, Michael J. Wilkins, Brian L. LaMarche

◆ We aim to develop chemical or activity-based proteomics probes and bioinformatics approaches for discovering enzymes relevant to biofuels production via insoluble cellulose degradation. These developments will be applied to measure the stability of cellulose degradation correlated to functional redundancy and environmental change. ◆

In nature, an important service provided by microbial communities is the breakdown of cellulosic biomass. Understanding how microbial communities perform this process improves our knowledge about how biofuels are produced. Unlike a single microorganism, microbial communities work synergistically, often because multiple populations within the community can perform the same process. The number of enzyme catalysts capable of carrying out the same function but produced by different populations in the community is known as functional redundancy. The general belief is that functional redundancy is critical to the stability of important processes in nature, such as cellulose degradation. Given an environmental upset, functional redundancy acts as a "buffer," allowing the community to continue to degrade cellulose.

Roughly 70% of plant biomass is composed of 5- and 6-carbon sugars, making it a primary resource for the development of second-generation biofuels. The enzymatic make-up and redundancy of these enzymes within a microbial community provide stability and synergism for the breakdown of recalcitrant cellulosic material. Measuring the redundancy of cellulose degrading enzymes within a microbial community presents a challenge in that convergent evolution has produced many enzymes capable of this activity but have dissimilar genomic sequence homology. We focus on a solution to determine empirically the redundancy of cellulosic enzymes through the development of proteomics probes that bind irreversibly to the active site of these enzymes. Enrichment of the enzymes and analysis using mass spectrometry will allow for the discovery of novel cellulose degrading enzymes and provide a means for measuring the redundancy of these enzymes within a microbial community.

Specifically, we are developing methods to measure the amount of functional redundancy associated with microbial communities housed in bioreactors capable of degrading cellulose. These measurements enable us to correlate the change in redundancy to cellulose degradation under sudden environmental upsets. Functional redundancy measurements are performed via chemical probes developed to imitate cellulose and irreversibly bind to the enzymes capable of degrading this substance. By placing a probe in a complex mixture of proteins harvested from a microbial community, cellulose-degrading enzymes that bind to the chemical probes are extracted and analyzed using mass spectrometry.

During FY 2010, six chemical probes were designed, with the first probe synthesized. While the first probe design is not original, working out the synthesis steps to make this probe was challenging and represents a breakthrough that will enable the synthesis of the remaining five probes. Initial testing against commercially available enzymes shows that the probe is specific to enzymes capable of breaking β-glycosidic bonds (that connect sugar [glucose] molecules together in cellulose) and has a high affinity for cellulose, as opposed to other carbohydrates. The probe was used to identify cellulose-degrading enzymes within bacteria recently isolated from a leaf cutter ant dump pile.

In FY 2011, a total of 13 probes were chemically synthesized. These probes have been designed to target glycoside hydrolysis activity generally and have anticipated specificity for exo-gluconases, endo-gluconases, and β-glycosidases. Several tests were carried out to evaluate each probe's specificity and selectivity. Testing was initially performed on commercially available glycoside hydrolase enzymes. While each probe varied in its specificity (labeling of a single enzyme to multiple enzymes), almost all showed general preference for enzymes that cleave β-glycosidic bonds.

Two cellulose degrading bacteria, *Clostridium thermocellum* and *Fibrobacter succinogenes* were selected to test the selectivity of the probes. Complex protein mixtures were extracted and successfully labeled using each probe, as indicated through visualization of fluorescent bands using SDS-PAGE. To confirm these results, mass spectrometry identification of the labeled proteins is in progress. An extensive analysis to identify all proteins from these cultures is also underway and will be used to gauge how well each probe is performing by comparison to the total glycoside hydrolase enzymes produced. To test these probes further, we are operating two laboratory scale anaerobic bioreactors, each housing cellulose degrading microbial communities acquired from biomaterial taken from the cow rumen. We plan to perturb each bioreactor, impacting the stability of cellulose degradation. It is anticipated that the amount of redundancy

associated with glycoside hydrolases before and after each perturbation will be measured using the probes, then correlated to the difference in cellulose degradation rates.

The analysis of mass spectrometry probe data is performed using MultiAlign, a software tool used to process liquid chromatography mass spectrometry data. Enhancements made to MultiAlign include a dataset to dataset alignment capability of mass and elution time features. To assess the "correctness" or strength of the aligned datasets, two scoring metrics were created that ultimately allow a judgment as to whether all common features represent the same peptide from glycoside hydrolases. These bioinformatics enhancements are significant in that they allow the proteomics analysis of microbial communities without the initial need of genomic sequence information.

	C. thermocellum		*F. succinogenes*	
Probe	Pellet	Media	Pellet	Media
GH1	X	X		
GH2a	X	X		
GH2b	X	X	X	
GH2c	X			
GH2d	X	X	X	X
GH4a	X	X	X	
GH4b	X	X		
GH5a				
GH5b				
GH6a	X	X	X	X
GH6b	X	X	X	X
GH7a	X	X	X	X
GH7b	X	X	X	X

X=Fluorescent bands observed from SDS-PAGE analysis.

Results from testing the selectivity of probes against model cellulose degrading bacteria. Tests were performed on microcrystalline cellulose (results shown) and glucose cultures (results not shown). Probes were applied to the total complement of proteins extracted from cell pellet and spent media fractions.

During FY 2012, these cellulase targeting probes will be applied to laboratory-maintained cellulose degrading microbial communities that will be perturbed in their ability to degrade cellulose. Perturbation experiments will be performed in an effort to correlate redundancy to shifts in degradation rates of cellulose, ultimately looking at the stability of a microbial community to degrade cellulose under environmental change. It is anticipated that the amount of redundancy associated with glycoside hydrolases before and after each perturbation will be measured using the probes and then correlated to the difference in cellulose degradation rates. In addition, these probes will be tested for their ability to bind to and enrich native cellulase enzymes from different environmental matrices, beginning with the soil environment. The action of native cellulases in the soil environment is a critical component in the cycling and sequestration of carbon.

Statistically Significant Forensic Fingerprinting: Protein Analysis of Biological Agents

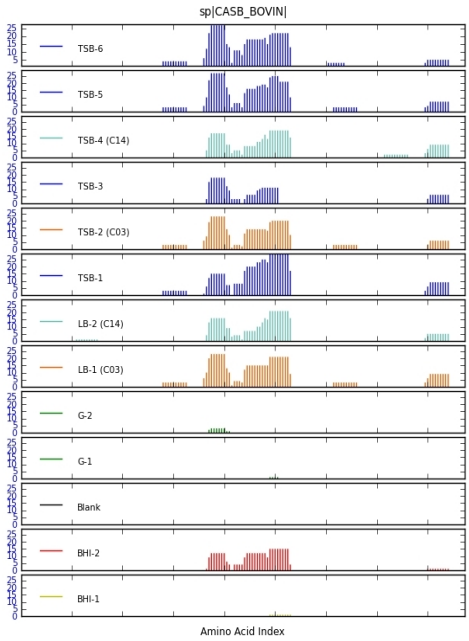
Brian H. Clowers, Aaron C. Robinson

◆ This effort aims to develop a method that provides a statistically relevant means of sample comparison using protein identification as an example application. ◆

Fundamentally sound statistical methodology is the foundation of any robust forensic method. While many different sample characterization approaches exist, difficulty in sample comparison is often encountered based upon domain specific analytical methodologies. This effort aims to develop a statistical comparison framework that integrates laboratory trials with an algorithm that directly identifies similar and dissimilar features between samples. Most importantly, the resulting methodology will provide forensic analysts with likelihood matching statistics between known and unknown samples while preserving many of the fine subtleties of the differences between samples. The merit of this approach will be demonstrated using a series of laboratory experiments aimed at supporting the bioforensics community.

This project will leverage the frequency of amino acid observation for known samples that will serve as the statistical basis to provide a likelihood of a match when screened against an unknown sample. This algorithmic approach to data relies on the frequency of observed features. Upon comparison, the weighted statistics of each feature provide a likelihood of a match between an unknown and laboratory-constructed fingerprint. While definitive matches are rarely obtained, the level of association between two samples can be assessed using this approach, and a broad range of statistically robust relationships may be constructed. One novel aspect of this computation is developing a new sample indexing method or hashing algorithm that seeks to identify statistically relevant matches across sample fingerprints.

In FY 2011, three potential biological threat agents were cultivated under differing conditions: inactivated and stored for future project work. Using a handling and data acquisition protocol designed to extract trace protein impurities, these samples provide core data used to characterize the forensic analysis approach. Sample analysis was also conducted with an emphasis on carbohydrate and lipid signatures. Because the goal is developing a robust statistical tool geared toward forensic investigations, we established a flexible database architecture capable of capturing a wide range of relevant data sets. While the capacity exists to accommodate a variety of data sets, the current database format has been optimized to incorporate raw and processed protein data and has the unique capacity to collapse results across different experimental classes. With this tangible database format, we examined a suite of hashing algorithms to develop an optimized matching scheme. These "similarity hashes" offer the benefit of rapid searching while returning statistically meaningful likelihoods.



Frequency histogram of observed protein signatures across different culture conditions. Each fingerprint highlights similar protein sources but not necessarily the same manufacturing source. Strong correlations exist between similar protein types demonstrating promise in a forensic setting.

Applying our matching approach to a database comprised of the protein frequency profiles for different organisms and their respective culture conditions, it was possible to distinguish between three different source conditions for an unknown organism. While successful matching was possible for a select class of organisms (gram negative), those that rely on culturing conditions with minimal protein content remain difficult to identify. This result confirmed the need to continue our integration of both lipid and carbohydrate profiles that will provide the discriminating forensic features.

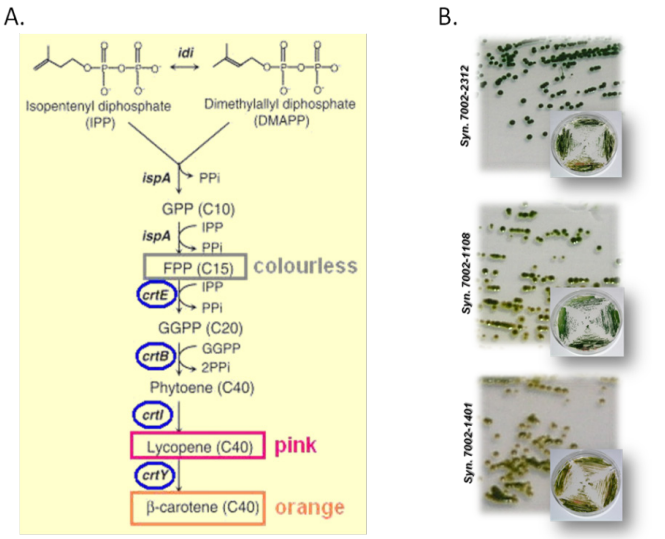
FY 2012 promises to deliver an accessible data analysis tool capable of integrated data from a variety of chemical analysis workflows. To accomplish this goal, data from lipid and carbohydrate analyses will be integrated into the forensic signatures database developed last year. Next, the similarity hashing algorithm will be optimized on previous results and tested against data to be acquired in FY 2012. To demonstrate the utility of this approach, we identified collaborators capable of providing an external source of truly unknown sample sets. By validating this approach with internal and external resources, our effort promises to expand PNNL capabilities and provide the bioforensics community a tangible forensic analysis tool built upon a sound statistically foundation.

Synthetic Biology Approach for Hydrocarbon Production in Microbial Photoautotrophs

Alex S. Beliaev

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

Using solar energy to grow photosynthetic microorganisms is one of the most attractive ways to produce transportation fuels. Among previously isolated species of microalgae exhibiting high potential for biofuel production is *Botryococcus braunii* race B (*BbB*), a green colonial microalga that isolated from a variety of habitats, including freshwater and brackish lakes, reservoirs, ponds, or even ephemeral lakes. This organism has considerable potential for production of lipids and liquid hydrocarbons that can constitute a large fraction of the total biomass. The typical hydrocarbon content of photosynthetically grown cells of *BbB* averages ~30-40% of the dry cell mass. Hydrocarbons extracted from the biomass of *BbB* can be readily converted to fuels such as gasoline and diesel by catalytic cracking or thermochemical liquification of biomass. While enhancing hydrocarbon production directly in *B. braunii* presents formidable challenges due to low growth rates, undeveloped genetic system, and lack of robust cultivation techniques, availability of genetic and metabolic engineering tools allow us to explore other photosynthetic organisms for hydrocarbon (triterpenoid) biosynthesis.



Engineering synthetic non-mevalonate pathway (NMP) in Synechococcus *7002: A. NMP provides precursor molecules for the biosynthesis of pigments (carotenoids) in cyanobacteria; B. Variations of C flux through the synthetic (isoprenoid biosynthesis) pathway can be seen in recombinant strains of* Synechococcus *7002 producing different levels of carotenoids.*

In this project, we applied a synthetic biology approach to reconstruct hydrocarbon biosynthesis in the fast-growing and genetically-manipuable cyanobacterial strain, *Synechococcus* PCC 7002, through optimization of genetic and metabolic controls within the host. The project also focused on understanding the growth physiology and triterpenoid biosynthesis in *BbB* for successful engineering of microbial photoautotrophs (i.e., cyanobacteria) for biofuel production. In addition to scientific goals, the project embodied technical objectives including development of cultivation methods, physiological techniques, and genomic approaches to studying the isoprenoid metabolism in microalgae and cyanobacteria.

As slow growth and microbial contaminants present major hurdles for the exploration of the biofuel potential of *BbB*, we concentrated our efforts in the first two years of this project on the identification of optimal cultivation conditions and factors inhibiting the growth of organism. As a result, we were able to optimize the photoautotrophic growth of *BbB* to where cells are growing with doubling times of about 48 hrs and display average density of 0.5 g DW/L biomass. We also optimized mass transfer in continuous cultures of *BbB* to enhance substantially the substrate (i.e., CO_2) delivery and byproduct (i.e., O_2) removal. Due to the accumulation of copious amounts of extracellular material, which encapsulates the cells of *BbB* and predominantly consists of secreted hydrocarbons, gas diffusion inside and out of the cell represents a key factor in controlling growth of the organism. In addition, we have developed methods for biomass collection using differential centrifugation which allows for efficient separation of *BbB* and bacterial cells.

To design and construct synthetic hydrocarbon-producing pathways, we used genome sequence and genome context analyses, to identify genes involved in isoprenoid biosynthesis (non-mevalonate pathway) in a wide range of green algae and cyanobacteria. An entire isoprenoid biosyntehsis gene cluster (total of 7 genes) have been isolated from a unicellular diazotrophic cyanobacterium *Cyanothece* sp. ATCC 51142

and cloned into a subset of expression vectors for functional and biochemical characterization. Individual genes as well as the entire isoprenoid biosynthetic pathway were introduced into a cyanobacterial host. Our organism of choice, *Synechococcus* PCC 7002, is a robust bioengineering platform, for which genetic system is available and a genome-wide metabolic model has been developed in collaboration with Dr. Bryant (Penn State). The metabolic reconstruction of pathways leading to production of farnesyl-PP, a key precursor for hydrocarbon biosynthesis, has been accomplished in 7002. Our approach for the engineering hydrocarbon-producing strain involved identification of reaction "bottlenecks" that allow for the increase of carbon flux through the non-mevalonate pathway. Using recombinant *Synechococcus* PCC 7002 strains, we over-expressed each isoprenoid biosynthesis genes and identified key enzymes that increase the production of carotenoids, which are one of the main end-products of the non-mevalonate pathway.

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

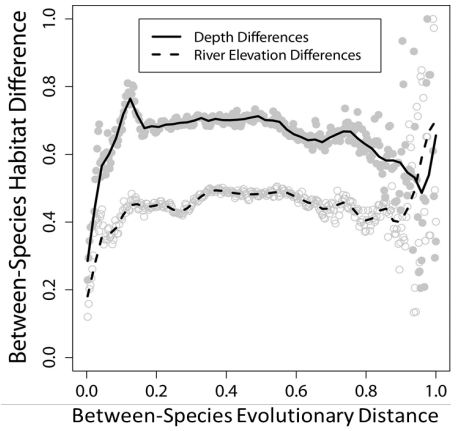
Understanding the Processes that Govern Subsurface Microbial Communities

James C. Stegen, Allan E. Konopka

◆ This project ultimately aims to develop theoretical tools capable of predicting microbial community composition and function through space and in response to environmental change. The resulting tools will be crucial for improving environmental and human health through remediation of contaminated sites across the United States and beyond. ◆

Microbial communities play a central role in the functioning of natural ecosystems by heavily influencing biogeochemical cycles. It comes as no surprise that microbes can influence human-derived environmental contaminants and efforts to remediate contaminated locations. It has also been repeatedly demonstrated that ecosystem function (e.g., elemental cycling) is strongly influenced by the composition of ecological communities. As such, if we are to understand how microbe-influenced contaminants move through ecosystems and how effectively to remove or stabilize contaminants, it is vital that we first understand what governs the composition of microbial communities.

Historically, ecological community research is descriptive (e.g., how many species are in a given area and how the number of species changes across locations). Current research focuses on the processes that govern observed patterns. Although useful, most contemporary studies only infer the dominant class of process. This approach fails to describe the constituent processes quantitatively necessary for developing predictive models. This project fills that void by coupling observational, experimental, and stochastic simulation approaches, using the Hanford 300 Area subsurface as a model system.



Vertical axis: difference in habitat preference between two species; horizontal axis: evolutionary distance between two species, where relatedness declines from left to right; solid line/closed circles: habitat characterized as subsurface depth; dashed line/open circles: habitat characterized as river elevation. The steep, initial increase in curves shows that closely related species have more similar habitat preferences.

The current project ran for only two months in FY 2011, with significant progress made by leveraging pre-existing datasets. These data were collected for 10 months (late 2009–mid 2010) at three locations across three depth layers. The project applied modern statistical tools to these data in order to characterize the phylogenetic composition of microbial communities in the subsurface of the Hanford 300 Area.

We first uncovered a novel pattern critical for interpreting microbial community analyses: more closely related microbial species have more similar habitat preferences. This is key for interpreting analyses of microbial phylogenetic community composition. We find that roles of specific processes vary spatially throughout the subsurface and time. Major processes include habitat matching (where each species grows best in a particular environment) and random effects (where any given species may randomly disappear from a community). A few general features such as depth and distance from the Columbia River determine relative influences of these two processes. If confirmed, this information will be used to develop predictive simulation models.

In FY 2012, we will focus on understanding community composition through space, and work towards predictive simulation models. A second pre-existing dataset from the Hanford 300 Area with good horizontal and vertical spatial resolution will be merged with geophysical data compiled by PNNL's Geosciences group. These data will support the development of a novel statistical model that predicts community composition through space. The key algorithm is being developed in collaboration with academic researchers, and will be tested with portions of the data not used in the training dataset. In addition, the spatial predictions will be coupled with a sample-gap analysis to define locations across the 300 Area in which new sampling wells would provide the most important and novel information.

Achieving the goals as outlined will represent a major step towards developing predictive simulation models of microbial communities. A currently available 2D spatially implicit simulation model will be modified to be specific to the 300 Area subsurface. This model will be used to predict microbial community composition across a variety of conditions. The most likely combination of community assembly processes will be estimated by comparing simulated patterns to our empirical data. The result will be the first empirically parameterized and empirically validated simulation model capable of predicting microbial community composition in the 300 Area subsurface through space, time, and in response to changing environmental conditions.

Chemistry

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

Zheming Wang, John S. Loring, Christopher J. Thompson, Alan G. Joly

◆ In this project, we are developing and demonstrating an in situ optical spectroscopy platform for investigating the molecular mineral transformation processes involved in carbon capture and sequestration and subsequently applying the techniques to study water dissolution and metal silicate carbonation reactions of capture- and sequestration-relevant minerals. ◆

The combustion of fossil fuels such as oil and coal has led to a rapid increase of CO_2 emission into the earth's atmosphere, which greatly contributes to global warming and causes adverse climatic and environmental changes. With global energy demand projected to increase by 57 percent by the year 2030, large-scale greenhouse gas emissions will continue and even accelerate. Carbon capture and sequestration in oceans and deep geological formations such as underground saline formations, unused oil wells, and mining seams has become one of the most promising strategies to store the freshly generated CO_2. From high temperature and pressure sustained in deep geological "vaults," CO_2 is predicted to remain for hundreds of years, which has a significant potential for reducing energy- and industrial-sector emissions of CO_2 into the atmosphere. For the duration of storage, $scCO_2$ will interact with saline solutions and electrolytes in the liquid phase and may facilitate significant mineral transformation.

The effectiveness of geologic sequestration and its sustainability at large scales depends in part on the reactivity of $scCO_2$ and the minerals in the hostrock and caprock. The nature and amount of the resulting secondary minerals and the extent and rate of CO_2 conversion are influenced by numerous chemical and environmental factors. Unfortunately, little is known about the physical and chemical processes that occur with $scCO_2$ and water at solid-liquid and liquid-liquid interfaces. The available thermodynamic database includes mostly aqueous phase phenomena with a limited amount of organic solvent data. Moreover, the scientific community lacks the necessary experimental infrastructure to address these complex issues, either at a process level or molecular level.

To address these deficiencies, we will develop an integrated supercritical fluid-optical spectroscopy system, including ultraviolet-visible absorption spectroscopy, laser-induced time-resolved fluorescence spectroscopy, Fourier transform infrared spectrometry (FTIR), Raman, and nonlinear optical spectroscopy (second harmonic generation and sum frequency generation). The developed system will be capable of performing in situ optical spectroscopy measurements of mineral dehydration, dissolution, formation, sorption and desorption, and characterization of the solid-liquid and liquid-liquid interfacial processes at temperature and pressure conditions relevant to carbon capture and sequestration.

During the first two years of the project, we developed two prototype supercritical fluid manipulation systems capable of optical spectroscopy measurements. Both platforms can operate from room temperature to 75°C, pressure up to 274 bar, and have features such as water vessel inline/offline, $scCO_2$ online dehydration, and thermostated reaction/observation cell and $scCO_2$ circulation lines. We also developed separate reaction vessels for attenuated total reflection FTIR and optical spectroscopic measurement. Using one of the systems, we investigated H_2O/D_2O dissolution and speciation in $scCO_2$. The results showed that H_2O and D_2O have unique infrared spectral features over a broad spectral range in $scCO_2$. A detailed analysis of the H_2O/D_2O spectra helped reveal the mechanism of water interaction with $scCO_2$.

In FY 2011, we employed in situ mid-infrared spectroscopy to follow the reaction of minerals at 4-hour intervals using water concentrations for variable saturation. Little discernable reaction occurred when the minerals were exposed to neat $scCO_2$, and a large dependence of reactivity on water concentration and the presence of liquid water on the forsterite particles occurred. For forsterite at 47% and 81% saturation, an Angstrom-thick liquid-like water film was detected on the mineral particles, and less than 1% of the mineral transformed. Most of the reaction occurred within the first 3 hours of exposure to the fluid. At 95% saturation and with an excess of water (36% above saturation), a nanometer-thick water film was detected, and the carbonation reaction proceeded continuously with approximately 2% and 10% conversion, respectively. Similar results observed for antigorite and brucite.

For the 54% and 93% saturation experiments, the dominant spectral features for antigorite are a) a broad O-H stretching band at about 3380 cm^{-1} arising from a thin film of liquid-like water on the mineral surface, b) a residual from incomplete subtraction of monomeric water combined with an HOH bending mode of liquid water at 1640 cm^{-1}, and c) a broad band centered at 1436 cm^{-1} due to the C-O stretching bands of a magnesium carbonate precipitate. Most of the reaction appeared to occur within the first 8 hours of the

below-saturation experiments. In the excess-water experiment, all of these features are more prominent, and the two C-O stretching bands (1425 and 1480 cm^{-1}) are distinguishable from each other. Additionally, the broad, positive-going feature between 1050 and 1270 cm^{-1} is evidence for what is likely an amorphous SiO_2 precipitate. We estimate that about 1% of the mineral was transformed to a carbonate phase and amorphous SiO_2, based on the decrease in absorbance in the forsterite Si-O stretching region at approximately 1039 cm^{-1}.

For brucite, higher water concentrations and higher temperatures led to greater brucite carbonation rates and larger extents of reaction. Hydrated carbonation products were found to be less prevalent than anhydrous forms with increasing water concentrations in the $scCO_2$. The only observed carbonation product at 35°C was nesquehonite ($MgCO_3 \cdot 3H_2O$). Mixtures of nesquehonite and magnesite ($MgCO_3$) were detected at 50°C, but magnesite was more prevalent with increasing water concentration. Both an amorphous hydrated magnesium carbonate and magnesite were detected at 70°C, but magnesite predominated with increasing water concentration. Similar to forsterite and antigorite, little or no detectable carbonation was observed when brucite was reacted with neat $scCO_2$.

This research has successfully demonstrated in situ spectroscopic observation of the conversion of forsterite, antigorite, and lizardite into carbonate phases when the minerals were exposed to wet $scCO_2$ for 24 hrs. A liquid water film appears to play an important role in the reactions. In the end, brucite and forsterite were significantly more reactive than the serpentine minerals. Our collective results ultimately suggest constitutive links between water concentration, water film formation, reaction rate and extent, and reaction products in wet $scCO_2$.

Characterization of Energy Storage Systems Using In Situ and Ex Situ Nuclear Magnetic Resonance Spectroscopy

Jian Zhi Hu, Vijayakumar Murugesan, Liyu Li, John P. Lemmon, Hardeep S. Mehta, Jiguang (Jason) Zhang

◆ We propose to develop unique in situ nuclear magnetic resonance (NMR) capabilities, including the application of existing developed techniques, to advance the understanding of the complex electro-chemistry, the ion transport mechanisms and the performance degradation mechanisms in the electrodes, electrolytes of stationary batteries, and Li-ion and Li-air batteries. ◆

Large-scale stationary energy storage is needed for the widespread use of intermittent renewable energy and for improving the quality of power management in modern electrical grid. For long-term large-scale applications, the ultimate cost of the storage technology and system should be less than $150/KWh with a life time greater than approximately 10–15 years (more than 2000–4000 charge discharge cycles) and is safe for operation. Currently, none of the known technologies has reached these combined goals. Revolutionary breakthroughs in both battery development and fundamental research are needed. Electrochemical storage has been recognized as one of the top choices for large-scale energy storage devices. Stationary batteries usually involve aggressive electrochemical environments such as concentrated electrolyte solutions in redox flow battery (RFB) and molten salts in sodium-metal halide battery, combined with rather complex electrochemical reactions and have been optimized using empirical methods and thereby require greater understanding to meet performance and cycle life goals to obtain market penetration.

We propose to develop unique in situ NMR capabilities to study the detailed redox chemistry and the performance degradation mechanisms in the electrolytes, membranes, and electrodes of stationary batteries, with a particular emphasis on flow-batteries Li-ion and Li-air. Advanced NMR spectroscopy with a wide range of magnetic fields from 7.05 to ultra-high field of 21.1 Tesla as well as NMR computational and modeling capabilities will also be employed to understand the complex chemistry. This combined investigation will yield detailed molecular information regarding ion transport mechanisms and the chemical status of the ions both inside the electrodes and at the electrode-electrolytes interface. This is especially important for the development of new stationary batteries with improved energy and power densities, and improved, long-term stability for electrochemical energy storage systems.

Redox flow battery (REB). During FY 2011, we carried out comprehensive ex situ multi-nuclear, including ^{17}O, ^{51}V, ^{1}H, ^{29}Si and ^{35}Cl, NMR investigations and temperature in situ multi-nuclear NMR studies on novel electrolytes and membranes associated with V-RFB. The goals are to understand the mechanisms of performance degradation at elevated temperature. Our findings have been summarized in four journal articles. In particular, our studies offered a molecular level understanding of the solution specification and thermal stability of mixed acid solutions that led to a 70% increase in energy density in V-RFB.

Li-ion and Li-air batteries. We made significant progress in understanding the ion transport mechanisms in both Li-ion and Li-air batteries, such that our research and activities have resulted in two articles published in the *Journal of Power Sources*.

In situ NMR capability development. An in situ static NMR probe for the investigation of a live Li-ion battery has almost been developed where a cylindrical plastic battery has been designed and constructed. The design of this same static probe also allows in situ investigating the detailed electro-chemistry in electrolytes of Li-air battery under real word operating conditions. Further, the concepts for developing a first of the kind in situ magic angle sample spinning (MAS) NMR probe for significantly enhanced spectral resolution on a live Li-ion battery has been formed. It should be emphasized that despite its wide spread application, magic angle spinning of a live battery has never been achieved. Associated technical challenges are self-evident as metals such alumina foil must be used as the current collectors in a live battery. Spinning a bulk metal in a strong magnetic field inevitably generates a strong eddy current that produces a strong force against the spinning, making fast sample spinning impossible if a regular battery is used. Our design will for the first time realize in situ MAS NMR detection on a live battery.

Our goals for FY 2012 include the following tasks. We wish to complete the in situ static NMR capability development. We will also strive to realize and demonstrate the first-of-the-kind in situ MAS NMR capability, using Li-ion battery as an example. While continuing the computational modeling of NMR shifts of battery materials, we will also pursue the temperature in situ and multi-nuclear NMR investigations on the electrolytes from flow batteries.

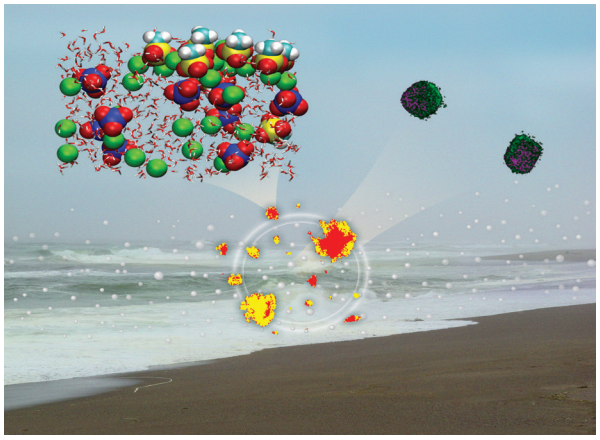
Chemical Imaging Analysis of Environmental Particles

Alexander Laskin, Alla N. Zelenyuk, John E. Shilling; Mary K. Gilles, Kevin R. Wilson (ALS/LBNL)

◆ This research will establish a unique analytical platform for comprehensive analysis of gas-particle reacting systems, and contribute to our collective goal of achieving a fundamental understanding of the chemical composition, reaction mechanisms, and kinetics of gas-particle transformations and heterogeneous chemistry pertinent to atmospheric and occupational environments. ◆

It is of great interest to understand how the chemical and morphological microstructure of environmental particles affects their physicochemical properties such as chemical reactivity, and thermodynamics of gas-particle systems, hygroscopic and optical properties of aerosols. Fundamental understanding of these properties and their possible evolution in time requires advanced analytical approaches for chemical imaging of particles on the scale of 10-100 nm in reactive environments. Environmental particles are multi-component and, therefore, a detailed understanding of their complex chemistry will reduce uncertainties related to their environmental effects. The application of complementary analytical methods is needed to provide comprehensive information, ranging from microscopy level details of individual particles to advanced molecular characterization of complex molecules comprising particulate matter. Particular attention is given to the application of a range of analytical techniques to experimental studies of heterogeneous gas-particle reactions pertinent to atmospheric and occupational environments, technologies related to energy production and emissions control, and particle health effects.

This project focuses on development of complementary experimental setups that allow chemical imaging of changes in particle morphology and composition in reactive environments. The research and development efforts will be carried out along two major directions: the development and application of micro-reactor cells for in-situ studies of gas-particle reactions using complementary methods of spectro-microscopy, and the development and application of particle depth-profiling methods by single-particle mass spectrometry. Our laboratory studies will investigate the relationship between particle morphology, composition, formation, reactivity, and evaporation by developing novel methods for chemical imaging analysis. The aim will be the size, morphology, and internal compositions pertinent to the heterogeneous chemistry of organic and soot particles over atmospherically relevant conditions of particle sizes,



Complementary methods of multi-modal chemical imaging and molecular dynamics simulations have been applied to study internal structure, hygroscopic, and reactive properties of mixed sodium methanesulfonate-sodium chloride particles.

concentrations of gas-phase reactants, atmospheric pressure, and relative humidity.

During FY 2011, we successfully accomplished several tasks. First, we evaluated the utility of depth-profiling approach by single particle mass spectrometry. The approach was applied for chemical imaging analysis of soot particles generated at different combustion conditions. Preliminary data indicate that the soot particles generated at different temperatures have remarkably different physical and chemical properties. Complementary off-line high-resolution mass spectrometry analysis of soot samples allowed us to provide molecular speciation of the aliphatic compounds. The presence of these compounds may affect the mechanism and kinetics of soot oxidation in a way that is currently not understood. The image shows internal structure, hygroscopic, and reactive properties of mixed-sodium chloride particles. Along with our initial studies, this likeness was featured on the cover of the journal *Physical Chemistry Chemical Physics*.

We were successful in securing access to the Advanced Light Source synchrotron facility. Our planned experiments include integration of single-particle mass spectrometer with vacuum ultraviolet light source for soft ionization of particles and in-situ hydration and gas-particle reaction studies using x-ray microscopy line. We have already conducted a number of laboratory studies focused on the chemistry of individual particles, where we demonstrated critical need for the methods of chemical imaging analysis for fundamental understanding particle internal structures and their effects on

hygroscopic properties, heterogeneous reactivity, and ice nucleation properties of complex, internally mixed particles.

During FY 2012, we will work on the design and fabrication of micro-reactor cells for use in spectro-microscopy studies. Using these cells, we will conduct experimental studies on chemistry of organic particles reacting with atmospheric oxidants. In parallel, we will continue development and applications of single-particle mass-spectrometry interfaced with the synchrotron VUV light source. Complementary capabilities of developed analytical techniques will be used to study chemical and morphological changes of organic particles produced in PNNL's environmental chamber.

CO_2 Separation Scale-Up

Dale A. King, Kriston P. Brooks, Feng Zheng

◆ This project aims to develop a flexible, modular, mobile CO_2 capture material test capability and evaluate the performance of novel PNNL capture materials against the goal of 20 percent reduction in energy consumption for flue gas CO_2 capture relative to conventional baseline materials. ◆

Currently available technical approaches for CO_2 capture include pressure swing adsorption (typically with liquid- or methanol-based solvents) and capture of CO_2 by liquid adsorbers such as monoethanolamine (MEA). These technologies for CO_2 capture operate at room temperature or below, are costly, and require substantial swings in temperature and pressure. The high cost results from two key factors: the low mass fluxes in the separation units and the high energy consumption during regeneration of the separation agent. For non-pressure swing adsorption approaches, the cost of the separation agent (notably MEA), its operating life and selectivity, and the complexity of the MEA process are also important factors in making any process economically attractive. New technologies that can enable separate or simultaneous economic removal of CO_2, H_2S (and COS), and Hg over a range from room temperature to temperatures compatible with the shift reactors can improve the economic viability of coal-based electricity and fuels in the United States.

A drawback of the ability to develop new, cost-effective means of CO_2 capture from fossil fuel sources is the limited capabilities for testing materials under a relevant operating regime, including representative impacts on material attrition and performance over life. Developing capabilities for the most promising CO_2 capture technologies and testing them on a larger scale in a CO_2 capture test laboratory is a principal goal. To meet this need, there are several different CO_2 capture technologies under development that are primarily differentiated by liquid or solid phase adsorption. The liquid phase processes can be distinguished by the method of regeneration—thermal or pressure swing versus electrochemical. For post-combustion capture, currently the highest priority, MEA can be used as a baseline technology against which the liquid phase LDRD CO_2 capture projects will be compared. We envision that a continuous process should have the ability to be demonstrated that has at least a 20 percent energy savings relative to the MEA process and operating the system so that at least 90 percent CO_2 is captured throughout the duration of the absorption test. For the case of solid adsorbents, the performance baseline standard is zeolite 13x, which as a 20 percent energy saving for the novel adsorbent processes relative to this standard and 90 percent CO_2 uptake over the duration of the adsorption cycle.

The CO_2 capture test capability developed under this project in 2010 consisted of three primary test systems: a wetted-wall column, a continuous-scale solid sorbent test cart, and a continuous-scale liquid solvent test cart. All three capabilities are applied in the context of a CO_2 capture material screening (TRL Gate) methodology to evaluate the viability of material candidates using progressively more comprehensive performance data and more representative operating conditions. In FY 2011, these test systems were refined and used to characterize the performance of baseline CO_2 capture materials over extended periods of operation. This set of test hardware and methods brings a unique capability for testing materials in larger quantities and at increased scale as material development efforts (by PNNL or others) progress toward engineering-scale testing.

Early in the development and selection of liquid solvents, more fundamental material parameters such as reaction kinetics and CO_2 loading capacities are evaluated using the wetted-wall column. Similar methods (developed separately) are applied to solid sorbents for fundamental material characterization. Following initial screening (and once higher quantities of materials are available), the continuous-scale test carts enable characterization under industrially relevant operating conditions and through large numbers of loading/regeneration cycles. During testing on the wetted-wall column, solvent flows downward along the circumference of a vertical metal column with CO_2-containing gas flowing upward around the column. This apparatus enables a very well-controlled interface area between the solvent and the gas. By monitoring gas composition changes after flowing past the wetted column perimeter, relationships describing sorption kinetics can be developed. The wetted-wall column was used in FY 2011 to collect detailed kinetic and equilibrium data on MEA and MDEA solvents. It was also used on a related project, teamed with Akermin to characterize potassium carbonate with mobilized enzymes.

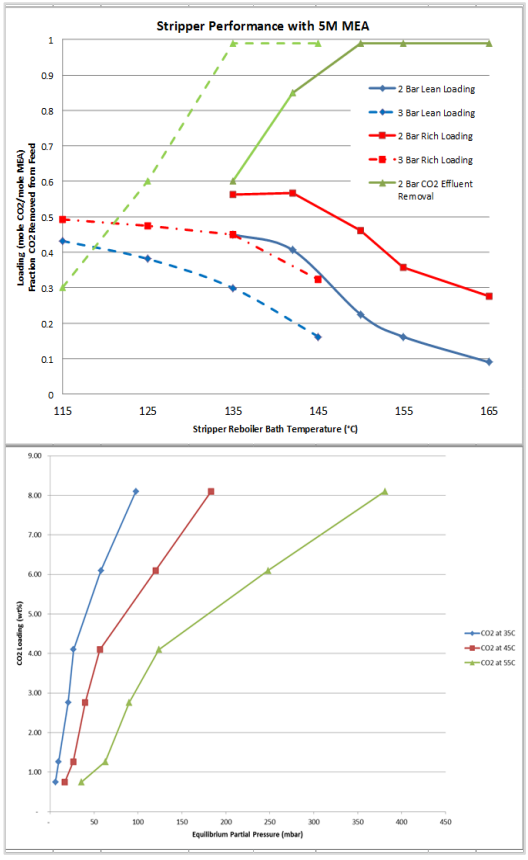
The continuous-scale solid test cart consists of two reactors that are filled with a material candidate in a packed-bed configuration. Inlet gas composition simulates a coal flue gas through the use of a set of bottled gases, mass flow controllers, and a gas saturator. A mass spectrometer is used to sample continuously the composition of the reactor outlet to enable characterization of loading profile and breakthrough characteristics. Reactor beds can be regenerated using thermal swing or pressure swing approaches, or a combination of the

two. The two-bed approach allows us to explore configurations expected to be necessary to achieve the anticipated CO_2 capture and purity levels requirements. In addition to gas compositions, bed temperature profile and pressure drop are monitored through the loading and regeneration steps. After completing the solid cart in FY 2010, it was used to characterize performance of zeolite 13X as a baseline data set.

For liquid solvents, the continuous-scale solvent test cart includes both absorber and stripping columns. Liquid sorbent candidates are routed through the contactor to absorb CO_2 from a simulated flue gas or actual flue gas. Solvent can be continuously loaded by circulating through the absorber alone or can be routed through a heat recuperator before routing through the CO_2 stripping column, as would be done in a full-scale process. Trim heaters and coolers are incorporated at the inlets of both columns for precise control over operating conditions. The stripping column has a reboiler for desorption of CO_2 from the solvent as well as a condenser at the top of the stripping column to remove solvent from the CO_2 stream prior to exhaust. As with the solid cart, performance of the material and process are monitored via mass spectrometer analysis of the product gas streams from both columns. The solvent cart was in the final stages of assembly at the end of FY 2010.

In addition to the wetted-wall solvent characterizations, work in FY 2011 completed a variety of system shakedown and material performance testing on the solid and liquid test systems. The solid sorbent cart was used to characterize the performance of zeolite 13X in a dual-bed configuration, using both thermal and vacuum swing regeneration. Because the performance of zeolites tends to be affected adversely by the presence of water in the flue gas, both dry and humid gas testing was conducted to quantify the impact of water. The solid sorbent cart was also tested at the flue gas testing facility at the PGE coal plant in Boardman, Oregon. The solvent cart was used in multiple campaigns both in the Sigma V carbon capture laboratory and off site at the PGE coal plant on actual flue gas. All testing used 5M MEA to establish standard test protocols and enable comparison with MEA performance reported in literature.

In addition to the cart testing, initial conversations and preliminary planning for testing at the National Carbon Capture Center (NCCC) were completed. The purpose of this testing will be to further enhance the capability to test solid and liquid capture materials in plant-relevant operating conditions and with either simulated or actual flue gas streams. This will increase PNNL's experience implementing early TRL material assessments and facilitate opportunities to interface and collaborate with material and process developers within industry and government. To enable off-site testing, an enclosed trailer will be retrofitted to house the test carts and serve as a mobile laboratory. The trailer was purchased by an unrelated project that has since been closed out and is available for retrofit. These retrofits and additional testing at PGE Boardman and at the NCCC will be completed during FY 2012.



Example sorbent performance data from test carts: CO_2 removal performance of MEA (top) and example solid sorbent isotherms (bottom).

Additional refinements to the test carts will also be performed in FY 2012, including upgrades to the solvent cart to enable more accurate, real-time measurements of reboiler duty and enhanced column liquid level sensing. Other work to be completed during FY 2012 includes enhancements to the PNNL combustion gas test platform, developed in prior years under a separate project to support testing with the continuous-scale test carts. Limited capture material testing with the combustor will be conducted to establish a baseline set of procedures and operating window for the combustor/test cart combination.

Computational Studies of the Transport and Thermodynamic Characteristics of a Variety of Gases in Ionic Liquids

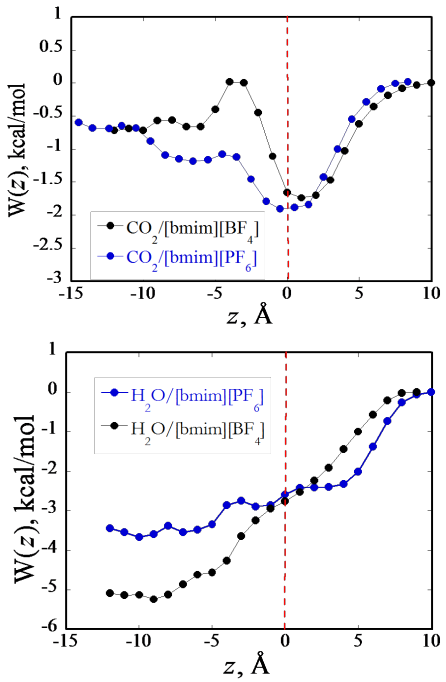
Liem X. Dang

◆ This research will help us better understand gas sorption and transport in existing room temperature ionic liquids (RTIL) and compare gas sorption with experiments. The long-range goal is to propose novel RTIL combinations and test their gas sorption properties and dynamics computationally without the need to synthesize them. ◆

RTILs have great potential to serve as new solvents for a variety of processes due to their unique properties and the ability to customize those properties by changing their substituents. The liquids include a cation and anion, each of which can be modified to form nearly countless combinations. Because of the near infinite possibilities, a better understanding of what promotes the high sorption and selectivity and optimizing gas transport would assist the design of new RTILs for specific gas sequestration. Computational methods allow a molecular-level understanding of gas RTIL interactions and how they promote greater selectivity and sorption, gas transport, and the ability to model systems without the need for synthesis. These benefits can be realized only if computational methods can be verified against existing systems. Given these challenges, we propose to develop the computational methodology to understand gas transport in RTILs, including their interfaces with air and other solvents, the factors that influence gas sorption and selectivity, and compare computed results with the experiment wherever possible.

To understand RTIL's interfacial structure and how it influences gas sorption and selectivity, we performed molecular dynamics simulations with many-body interactions in FY 2010 to determine the mechanism for CO_2 and SO_2 solvation in butyl-methylimidazolium borate (BMIMBF4). New polarizable force fields were developed for BMIM, BF4, and CO_2 and gave good agreement with experiment for the BMIMBF4 liquid density and reasonable agreement with the experimental BMIMBF4 heat of vaporization. Comparisons with the experimental surface tension and x-ray reflectivity at the air-BMIMBF4 interface also showed good agreement. Additionally, our results showed that the nanostructured ordering in the RTIL creates pockets of enhanced CO_2 and SO_2 solubility, and our potential of mean force (PMF) results illustrated the importance of the nanostructured interfacial structure on gas solvation.

During FY 2011, we performed simulations with polarizable potentials to determine how [bmim][BF_4] and [bmim][PF_6] differ in their ability to absorb H_2O and CO_2. The PMFs for CO_2 across the air-[bmim][BF_4] and air-[bmim][PF_6] interfaces are viewable, with the Gibbs dividing surface (GDS) position having an uncertainty of around 1 Å. The difference between the gas and average liquid value can be used to estimate the free energy of solvation and compared with values extracted from experimentally measured Henry's laws coefficients. The free energies extracted from the simulations appear to estimate a free energy of solvation (-0.6 kcal/mol for both systems) between 0.2-0.5 kcal/mol, which is too low, but the uncertainty in the PMFs calculated from four independent simulation blocks is ~0.4 kcal/mol, around the uncertainty limit of our simulation results. The PMFs become negative farther out for the [bmim][BF_4] system, but this could be due to the uncertainty in the GDS position.

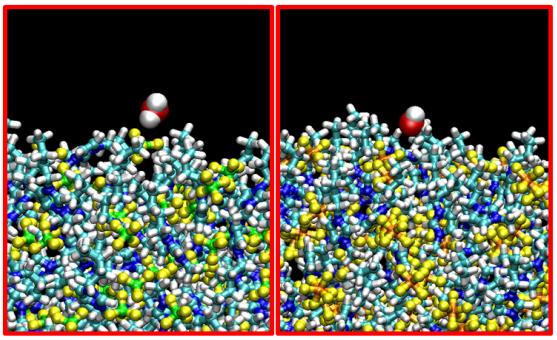


Calculated PMFs for CO_2 (upper) and H_20 (lower) molecule transport across the air-[bmim][BF_4] and air-[bmim][PF_6] interfaces.

CO_2 has a free energy minimum at both interfaces of around -1.8 kcal/mol, which has been attributed to the enhanced [bmim] alkyl density in this region. In the region from 2-6 Å from the GDS toward the liquid, there are increases in the free energy for both systems, in the region where the [bmim] ring has its highest density, but it is much more pronounced for the [bmim][BF_4] system. Favorable interactions between CO_2 and fluorinated anions is why CO_2 has reasonably good solubility in RTILs. The [bmim][PF_6] system shows weaker oscillation between [bmim] and its anion than the [bmim][BF_4] system does. Because of this, the CO_2 PMF would be expected to show greater oscillation in [bmim][BF_4] than [bmim][PF_6], as can be observed. It should also be noted that despite the long simulation times, some of the fine details of the PMF in bulk RTIL may

be influenced by the slow movement of the RTILs themselves, causing some oscillation that may disappear with much longer simulation times (on the order of 15-20 ns).

The H_2O PMFs were carried out using the same parameters similar to the CO_2 system. The free energy of solvation for H_2O is estimated by the difference between the bulk and gas phase free energies in the PMF, which are compared with free energies derived from experimental Henry's Law coefficients. The values between the simulation and experiment are in excellent agreement, within the estimated uncertainty of the simulation results of 0.4 kcal/mol. The free energy of solvation in [omim][BF_4] is much lower than in [omim][PF_6], due to stronger interactions with the [BF_4] anion than with [PF_6]. Despite this, the PMF decreases farther away from the GDS towards the air at the air-[bmim][PF_6] interface than for [bmim][BF_4]. After reaching 5 Å from the GDS of the air-[bmim][PF_6] interface, the free energy decreases only slightly as a H_2O molecules moves towards the bulk. This is unlike that observed at air-[bmim][BF_4] interface, in which the free energy decreases monotonically and rather sharply from the air until it is ~7.5 Å from the GDS towards the liquid bulk. The quicker flattening of the H_2O PMF at the air-[bmim][PF_6] interface is likely due to the weaker structuring at that interface in comparison with [bmim][BF_4].



Snapshots of water at the air-[bmim][BF_4] (left), and the air-[bmim][PF_6] (right) interfaces.

At the air-[bmim][BF_4] interface, the water molecule appears to hydrogen bond with the [BF_4] anion, which does not have a high concentration in the interfacial region as compared the corresponding [PF_6] anion. It would be expected that there would be some energy penalty associated with this, but it would be difficult to quantify. Further, there is enhanced density of the [bmim] alkyl groups at the air-RTIL interfaces for the two systems studied, with the alkyl group appearing to interact with the water oxygen. This would not be very strong interaction, as the alkyl group is fairly hydrophobic. Snapshots showed that at the air-[bmim][PF_6] interface, the only interaction is with the [bmim] alkyl groups in the snapshots, which are the prevalent species there.

In summary, molecular dynamics simulations were carried out to investigate the interfacial solvation behavior of CO_2 and H_2O at the air-[bmim][BF_4] and air-[bmim][PF_6] interfaces to determine the influence of the type of anion on interfacial solvation. The free energies of solvation for CO_2 and H_2O were in good agreement with experiment and showed similar CO_2 solvation, but [bmim][BF_4] had a much more negative free energy of solvation for H_2O. The water had a much higher interfacial free energy than in the bulk at air-[bmim][BF_4] than the air-[bmim][PF_6] interface, in which its interfacial free energy was of similar magnitude as in the bulk. This region coincides with the free energy profile of H_2O across the air-[bmim][BF_4] interface reaching a value similar to its bulk solvation free energy and increases as the H_2O molecule moves toward air. Our results show that H_2O is much more likely to be found at the air-[bmim][PF_6] than the air-[bmim][BF_4] interface. Our computed solvation free energies for CO_2 in the [bmim][BF_4] and [bmim][PF_6] liquids are almost identical, and these results agreed with measured data that the solvation free energies of CO_2 in both ionic liquids [bmim][PF_6] and [bmim][BF_4] are essentially identical. This work was published in and featured on the cover of *The Journal of Physical Chemistry B*.

Conversion of Biomass to Jet Fuels

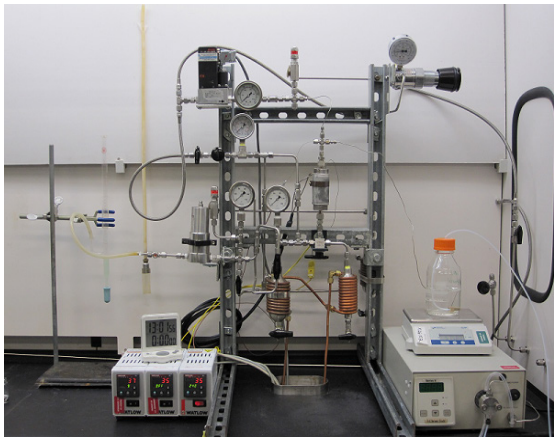
Karthikeyan K. Ramasamy, Yong Wang

◆ The aim of this project is to provide a fundamental understanding of the catalytic conversion of bioethanol to jet fuel range hydrocarbons, utilize the fundamental knowledge generated to design the catalysts to produce full-performance jet fuels from a wide range of biomass-derived low value oxygenates. ◆

Currently, all aviation fuel is derived from fossil sources. Due to the high interest level of the renewable fuel resources, currently Honeywell's is involved in developing a process to produce jet fuel from natural oil and algae resources. Jet fuel requires roughly 40 wt% of aromatic and cyclic content along with approximately 60 wt% of C_8 to C_{16} paraffinic (straight and branched) hydrocarbon due to stringent specifications such as low freezing point, high flash point and high volumetric density. In addition to the unfavorable cost, the above mentioned natural oil and algae processes produce only the paraffinic content of jet fuel and depends on other resources for its aromatic content.

We propose to study the elementary steps involved in the ethanol-to-gasoline conversion using a similar concept to the methanol-to-gasoline (MTG) process developed by Mobil. We will probe the nature of catalysts and design the catalysts with controlled morphology and structure to achieve the target activity and selectivity towards the product slate to meet the stringent jet fuel composition. The fundamental knowledge generated will be used to design the catalysts to achieve one pot synthesis to produce full-performance jet fuel from a wide range of biomass-derived oxygenates, including alcohols, carboxylic acids, and ketones. Successful outcomes from this project will not only lead to producing higher hydrocarbons from alcohols but also generate the knowledge base that can be used to develop processes to produce higher hydrocarbons from a wide range of biomass-derived low value oxygenates.

During FY 2011, our focus was on the conversion of ethanol to aromatic and the cyclic content of the jet fuel fraction. In this work, experiments were designed to understand the nature of the catalysts and the primary reaction mechanisms involved in the MTG-based process to achieve high jet fuel fraction with 100 percent carbon efficiency. At present, approximately 50 percent of the carbon present in ethanol goes toward jet fuel range fraction, with the remaining carbon ending up in the gasoline range fraction and light hydrocarbon gases.



Flow reactor setup for catalyst testing experiments.

Based on the literature information, initial baseline experiments were conducted in a flow reactor to optimize the operating temperature, pressure, and space velocity. Different alcohols (methanol, ethanol, and 1-propanol) and different families of zeolites (MFI, BEA, MOR, and FAU) were tested to understand the reaction mechanism and the nature of the catalyst towards jet fuel production from alcohol. Dominant liquid products from methanol, ethanol, and 1-propanol experiments are tetramethylbenzene, diethylbenzene, and dipropylbenzene, respectively. This is mainly due to the alkylation of benzene with the respective olefin (product of inter and intra molecular dehydration of alcohols). Among the zeolites tested, HZSM 5 (MFI family) was extensively studied due to its high activity toward the jet fuel fraction and its high resistance against catalyst deactivation through coking mechanism.

Catalyst properties, such as the silica/alumina ratio vary the catalyst acidity, metal impregnation to create bifunctionality, catalyst crystal size variation to change the residence time, post synthesis alkali treatment to modify the pore size, and silylation of external acid sites to reduce the cracking reaction were studied on the HZSM 5 catalyst. With this catalyst, close to 100% dehydration of ethanol is achieved at temperatures above 300°C. The highest liquid hydrocarbon yield was 360°C and 300 psig pressure. At optimized conditions, more than 60 wt% of the carbon present in the ethanol ends up in the carbon chain length greater than C_8 and it is dominated by the aromatic and naphthalene compounds. This can be partially hydrogenated to fit the aromatic and the cyclic content of the jet fuel.

The proposed work for FY 2012 will focus on the fundamental understanding of the catalytic processes involving ethanol dehydration followed by ethylene oligomerization (heterogeneous catalyst) to achieve the paraffinic (straight and branched) portion of the jet fuel. Additional effort will also be given to optimize the MTG-based process by means of modifying the catalyst and operating parameters to produce full performance jet fuel from one-pot synthesis.

Detection and Characterization of Uranium Hexafluoride Reaction Products in the Environment

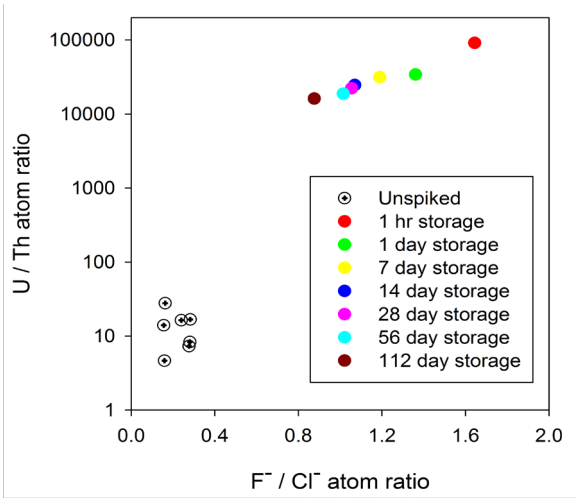
Steven C. Smith, Leah M. Arrigo, Bret D. Cannon, Herman M. Cho, Paul L. Gassman

◆ This project will attempt to develop new technologies for the detection and characterization of uranium hexafluoride (UF_6) and its reaction products in the environment. ◆

The need for new technologies to detect and characterize UF_6 and its reaction products in the environment has been identified and has nuclear forensic applications. This project will attempt to develop bulk chemical extraction, nuclear magnetic resonance (NMR), and fluorescence spectroscopy techniques to improve the fundamental understanding of the chemical behavior of uranium oxyfluorides and their reaction products when associated with environmental media. We seek to advance the current understanding of the environmental chemistry of these materials by exploiting the unique characteristics of this family of compounds to develop new methods for their detection and characterization.

Specifically, bulk chemical extraction of soils, NMR spectroscopy of solid and liquid materials, and cryogenic laser-induced fluorescent spectroscopy (CLIFS) techniques will be applied and evaluated. Bulk extractions will focus on the co-extraction of uranium, thorium, chlorine, and fluorine. NMR spectroscopy will characterize the fluorine-uranium chemical association using a new custom-built probe. The two issues addressed by CLIFS are line width-narrowing in aqueous solvents at cryogenic temperatures and exploration of the sensitivity of the cryogenic spectra to changes of the uranyl complex in nonaqueous solvents. A primary outcome of this project will focus on the techniques that leverage advanced analytical methods.

The bulk extraction task generated data that demonstrated the concept of perturbed element ratios in an extract may be useful for the detection of uranium oxyfluorides. Three exemplary soils were evaluated for this purpose, and useful data were obtained from one soil. Two series of experiments were performed: an evaluation of the impact of storage time on the extraction of uranium (U) and fluorine (F) from spiked soil and a determination of the method's conditional detection limit. As shown in the figure, perturbed U/Th and F/Cl atom ratios were detected in extracts of all treatments under the parameters of the experiment. Additionally, we demonstrated that increasing the storage period following the spike results in decreased extractability of both the U and F from the spike. These results establish some of the capabilities and limitations of the concept.



Experimental results illustrate the variation of uranium/thorium and fluorine/chlorine atom ratios in extracts of unspiked soil and soil spiked with UO_2F_2.

Initial results using CLIFS demonstrated the capability to obtain spectra of a 20 ng/mL U (as UO_2^{2+}) solution with high sensitivity and a signal to noise ratio of >100:1. Additional effort focused on investigating the behavior of the uranyl ion in solution with water and an organic solvent in various ratios. The results improved the fundamental understanding of the solvation and complexation of uranyl in this system. The time-dependent reaction of uranyl with a soil was also established. Reaction heterogeneity was observed and attributed to the complex nature of the mineral assemblage. This effort will assist with the development of extraction and analysis protocols that preserve uranyl chemical information.

A low-background magic angle spinning probe was designed and constructed to enable high resolution ^{19}F NMR measurements of radioactive materials in solid or solution samples. The probe was used with a 7.05 Tesla (300 MHz) instrument to calibrate the response of the device with variable amounts of aqueous phase F^-. A linear response was observed in the range from 0.02 to 1000 µg/mL F. Moreover, multiple U-F species were distinguished in a single aqueous sample. The probe was subsequently used with solid materials to investigate the chemical behavior of UO_2F_2 with these materials and provided insights into the reaction behavior of F in the model systems.

The new information and methods developed by this project will provide powerful, new analytical techniques that assist in the detection and characterization of UF_6 reaction products when associated with environmental media.

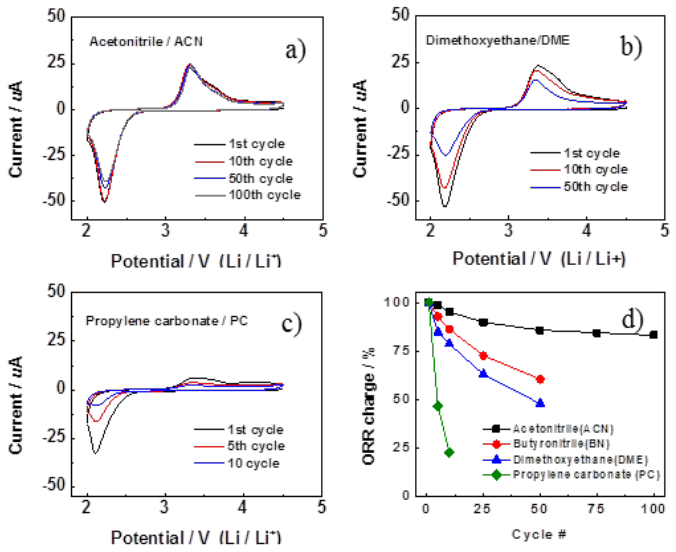
Development of Bifunctional Electrocatalysts for Rechargeable Lithium-Air Batteries

Yuyan Shao, Jie Xiao, Wu Xu

◆ The lithium (Li)-air battery is a transformational energy storage technology that can enable driving ranges of electric vehicles comparable to gasoline-powered vehicles. Developing advanced air electrode materials such as bifunctional electrocatalysts is critical for the advancement of this technology. ◆

The Li-air battery is at a very early stage of development. Its practical application is currently limited by its poor power capability, low energy efficiency and short lifetime due to the sluggish reactions of oxygen reduction and oxygen evolution in the air electrode. The fundamental study is carried out to understand oxygen reaction mechanism which is the prerequisite for Li-air battery development. Based on this idea, advanced bifunctional electrocatalysts for oxygen reduction and oxygen evolution in air electrodes are designed and developed.

The research under this project is providing a fundamental understanding of electrode reaction mechanisms and high-performance electrode materials for transformational energy storage and conversion systems. We aim to develop a new characterization platform based on a rotating disk electrode; a technology platform that will have the advantages of low cost, high throughput, simplified, and convenient operation. We will perform fundamental studies of oxygen reduction reaction mechanisms and oxygen evolution reaction in Li-air battery electrolyte conditions to provide a mechanistic understanding of this new energy system and guidance for electrocatalysts materials design/development. High-performance bifunctional electrocatalysts will be designed, synthesized, characterized, and integrated into the air electrode based on studies that increase understanding of oxygen reduction reaction and oxygen evolution reactions in combination fuel cell electro-catalysis research.



Cyclic voltammetry of glass carbon electrode in 1.0M Li ion containing electrolyte based on a) acetonitrile (ACN), b) dimethoxyethane (DME), c) propylene carbonate (PC), d) cyclability of ACN, butyronitrile (BN), DME, tetraglyme (4G), and PC. Acetonitrile shows the best cyclability, with the poorest being PC.

In FY 2011, we developed a new technology platform for mechanism study and electrocatalyst development. This new platform simplifies the study of oxygen reaction mechanism in simulated Li-air conditions. The platform also significantly accelerates electrocatalyst screening: the test time of one is a few hours compared with days or weeks in traditional test methods. Through these developments, we learned: 1) alkyl carbonate-based electrolyte are usually unstable, among which linear carbonates are slightly more stable than cyclic carbonates, 2) ether—like various glyme—based electrolytes are more stable than carbonates, among which short-chain ethers are more stable than the long-chain varieties, 3) nitrile-based electrolytes are the most stable one among all the studied nonaquoeus electrolytes. A stable electrolyte is critical for both oxygen reaction mechanism study and electrocatalyst development because all this work needs to be done in electrolyte. The electrolyte is one of the three key components (anode, cathode, electrolyte) of a Li-air battery and is, therefore, important for practical Li-air battery development.

In FY 2012, we will perform the following: 1) develop in-situ characterization tools (e.g., NMR, TEM, SME) for Li-air battery investigation; 2) optimize the stable electrolyte system; 3) study oxygen reaction mechanism using the newly developed technology platform with a focus on oxygen evolution process (i.e., decomposition of Li peroxide, which is critical for the charge process and energy efficiency of the Li-air battery); 4) identify the determining factors that limit the power density, energy efficiency, and cyclibility of air electrode; and 5) develop carbon-based electrocatalysts with a focus on low-cost materials such as chemically functionalized carbon and nanostructured metal oxides. The success of this project will provide the foundation of Li-air battery development and enable this transformational energy storage technology for practical applications.

Development of Inorganic Water Oxidation Electrocatalysts

Jenny Y. Yang, Daniel L. DuBois

◆ This project will develop new classes of homogeneous inorganic water oxidation electrocatalysts that improve upon the efficiency, rate, stability, and cost of known catalysts. With the use of highly modular ligands, this systematic approach toward catalyst discovery is expected to generate new families of effective water oxidation catalysts. ◆

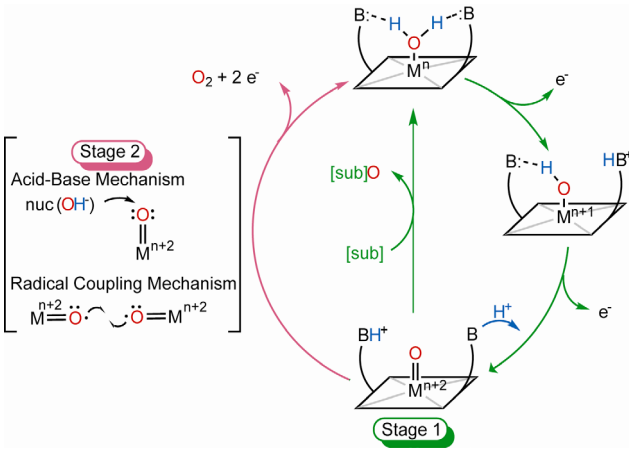
The development of a non-fossil fuel energy infrastructure is one of the major challenges facing our country for environmental, economic, and national security reasons. An answer to this challenge is the development of an artificial photosynthetic system. In nature, plants use sunlight to generate chemical fuels by reducing carbon dioxide and oxidizing water to evolve oxygen. A practical synthetic device would require an efficient, fast, and stable catalyst capable of oxidizing water under ambient conditions. Despite several decades of research, there are only a few examples of heterogeneous catalysts for water oxidation and most require the use of precious metals. Aside from expensive noble metals, current catalysts do not have the efficiency, speed, or stability to function on a practical scale. However, we know from nature that water oxidation can be performed under all of these conditions using cost-effective first row transition metals.

Our approach to catalyst design is to mimic the essential qualities from nature's architecture and incorporate it into synthetic systems. A critical consideration is energy-matching through the catalytic cycle using proton management. We use thermochemical measurements to assist catalyst design to approach the thermodynamic equilibrium at each step of the catalytic cycle. This is essential to maintain high efficiency. Effective proton management is also an important design element to avoid high or low energy intermediates in the catalytic cycle. Multi-electron and multi-proton chemistry is facilitated in nature by controlling the proton inventory at enzymatic active sites using amino acids. Our synthetic systems incorporate proton acceptors in the secondary coordination sphere to perform these functions.

We attack the challenging four-electron process to oxidize water by studying the catalytic cycle in two steps. The first stage will cover the two-electron oxidation of a water molecule bound to a complex to form a metal oxo species, the first intermediate in oxygen bond formation. This can be studied spectroscopically and chemically probed by oxygen atom transfer reactions. The second stage will couple the metal oxo intermediate with another metal oxo or hydroxide to initiate the evolution of oxygen and close the catalytic cycle. The intermediates and chemical steps in our catalytic cycle are consistent with mechanisms proposed for natural and synthetic systems that catalyze this reaction.

In the first year of the project, we explored a few different ligand classes, which provided valuable insight into future design and architectures. We found that ligand geometries that enforce open coordination sites are necessary to prevent the metal from chelating more than one ligand and saturating the metal. Also, better positioning and rigidity of proton relays into the ligand backbone were required to keep relays in the secondary coordination sphere instead of binding to the metal.

For FY 2011, two ligand systems were explored that fit the above requirements. The first is a modified porphyrin with pyridines incorporated in the meso position as proton relays. The iron complex does not appear to be active for water oxidation. However, the reverse reaction (oxygen reduction) was explored by the University of Washington and is a highly active electrocatalyst that demonstrates high selectivity to the reduction to water. The second ligand system currently being explored are five-coordinate pyridine ligands (Py5). The complexes $[(Py5)M(H_2O)]^{2+}$ and $[(Py5)M(OH)]^{2+}$ (M= Fe, Co) have been synthesized, including a rare example of an Fe^{III}—OH complex. The proton coupled electron transfer from oxidation of the aquo complex and thermo-chemical properties are being studied. Analogous complexes that incorporate proton relays are currently being synthesized.



Outline of the catalytic cycle. Stage 1 shows the formation of the metal oxo probed by reaction of an easily oxidized substrate; Stage 2 initiates the oxygen bond formation with the reactive metal oxos.

For FY 2012, we will map out the thermochemical properties of the relevant intermediates in the catalytic cycle. We will expand on our studies of electrocatalytic oxidation of water to perform oxygen atom transfer chemistry. We will use these results to improve the rate and efficiency of the catalysts, and initiate studies on oxygen bond formation.

Development of New Soft Ionization Mass Spectrometry Approaches for Spatial Imaging of Complex Chemical and Biological Systems

Julia Laskin, Ljiljana Paša-Tolić, Brandi S. Heath, Errol W. Robinson, Donald F. Smith, Zihua Zhu, Gordon A. Anderson

◆ Novel experimental approaches are essential to understand biochemical processes of interest for environmental cleanup, bioremediation, carbon sequestration, national security, and health sciences. We are developing complementary cutting-edge mass spectrometry (MS) imaging techniques that will enable mapping of chemical compounds produced by biological systems with unprecedented spatial and mass resolution. ◆

MS imaging is a powerful technique for obtaining a molecular-level understanding of chemical and biological systems. It offers a number of unique advantages for characterization of complex systems including high sensitivity, speed and unprecedented chemical specificity. The limitations of current state-of-the-art MS imaging techniques include sample pre-treatment prior to analysis, unwanted fragmentation of analyte ions, and limited spatial resolution as compared to optical and electron microscopy methods. The objective is to bring soft ionization, sensitivity, and unsurpassed chemical specificity of MS to the nanoscale and apply these novel tools for characterization of microbial biofilms. We are using *Shewanella oneidensis* biofilms as a model system for dissimilatory metal-respiring bacterial communities of interest to bioremediation and cleanup of contaminated DOE sites.

Shewanella has been extensively studied because of its potential use for cleanup of uranium and toxic metals. However, a mechanism of the extracellular electron transport in *Shewanella* biofilms responsible for metal reduction is still largely unknown. In the course of this project, we will develop approaches for comprehensive MS characterization of extracellular material in biofilms and obtain detailed spatial profiles of chemical gradients generated at interfaces between biofilms and mineral surfaces. Mass spectrometry imaging experiments of chemical gradients generated at oxidizing mineral interfaces will reveal the identity of extracellular redox molecules that facilitate electron transfer between cells and mineral surfaces essential for metal reduction by the biofilm. An integrated approach that combines complementary MS-based imaging approaches with optical and electron microscopy holds great promise to answer conclusively how microorganisms cycle metals such as Fe and Mn, catalyze acidification of metal-rich acid mine waste streams, and participate in the transformation of toxic metals such as U, Cr, Tc, and Pu.

To achieve these goals, we developed a novel platform during FY 2010 for ambient imaging of biological samples using nanospray desorption electrospray ionization (nanoDESI) MS. This method provides unique advantages for highly sensitive spatially resolved chemical characterization of biological samples in their native state. In nanoDESI, the surface is probed by a liquid bridge formed between two glass capillaries in contact with analyte deposited on a substrate. First, nanoDESI imaging experiments utilized biological tissues as model systems. We demonstrated highly sensitive ambient nanoDESI imaging with the spatial resolution better than 12 μm, which is 10 to 20 times better than the spatial resolution obtained using more traditional ambient pressure surface ionization techniques. We also demonstrated the utility of nanoDESI for sampling and direct analysis of living bacterial colonies, a unique capability of this MS imaging technique. In these experiments, bacterial biofilms grown on agar are analyzed directly from the growing medium without any sample preparation. This will enable detailed mapping of chemical signals generated by microbial communities in response to their environment, which is essential for detailed understanding of interactions between different microbial communities and between biofilms and mineral surfaces.

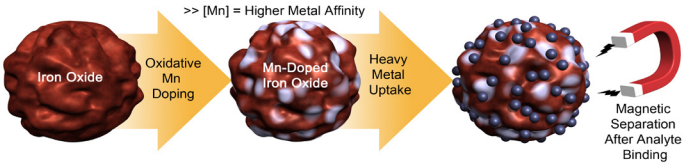
Complementary characterization of complex biological samples will performed using the novel C_{60} secondary ion mass spectrometry (SIMS) system coupled to a Fourier transform ion cyclotron resonance (FT-ICR) MS imaging apparatus constructed as a part of the EMSL recapitalization project. C_{60} SIMS is commonly used for sub-micrometer chemical imaging of organic and inorganic surfaces. However, SIMS is typically coupled to mass analyzers characterized by a relatively low mass resolving power (<5,000), which greatly complicates peak assignments. In order to alleviate this problem, we have coupled a high spatial resolution SIMS ion source with a high-resolution FT-ICR mass spectrometer. The one-of-a-kind C_{60} SIMS FT-ICR MS apparatus is characterized by high mass accuracy (<1 ppm), high mass resolving power ($m/\Delta m_{50\%}$ >200,000), tandem MS capabilities. This novel system was successfully used for imaging of tissue samples. The ability to resolve isobaric peaks in SIMS of biological samples is a key to characterizing chemical gradients present in such complex systems.

Future research will involve multimodal characterization of *Shewanella* biofilms providing unique insights on molecules responsible for electron transfer between cells and mineral surfaces.

Development of Novel Functionalized Iron Oxide and ZVI Nanoparticles for the In situ Capture and Decomposition of Aquatic Contaminants

Marvin G. Warner

◆ We aim to develop novel, functionalized nanoscale materials capable of selectively targeting environmental remediation-relevant toxic organic and metal contaminants in aquatic sediments as well as serve as interesting scaffolds for drug and radionuclide delivery. This was accomplished with methods we developed for functionalized magnetic iron oxide nanoparticles with high affinity ligands and Mn dopants. ◆



Under this project, we developed novel methods for the Mn-doping of iron oxide nanoparticles. Incorporation of Mn into the iron oxide nanoparticle lattice structure changes the surface chemistry and effectively tunes the affinity and specificity of the nanoparticle sorbent toward a variety of heavy metal contaminants.

The environmental and health issues associated with heavy metal- (i.e., Hg, Pb, Cd, etc.) contaminated waters have become more significant as population density and industrialization has increased globally. Further, the remediation of these contaminated waters has become progressively challenging as more information about their deleterious health effects pushes drinking water and effluent regulatory limits down to the low ppb level. An abundance of materials have been reported in the literature for the collection of heavy metals. While most of the reported materials have some advantageous properties, few sorbents can meet the feasibility, cost-effectiveness, recoverability, and toxicity requirements to be a viable option for treatment of wastewater systems. Nanomaterials and nanoparticles such as those developed in this project have seen increased attention for heavy metal remediation applications since the nanostructured surfaces offer large surface areas that provide enhanced capacity, as well as the ability to enhance contaminant affinity with chemical modification of the surface. Bare magnetite, maghemite, and examples of each of these iron oxide phases coated with affinity ligands or polymers have been used increasingly for the targeting of contaminants from wastewater. They are attractive candidates due to the oxides' inherent affinity for many toxic chemicals but have the added advantage that they are easily removed through magnetic manipulation.

Under this project, we developed a synthetic method for tuning the analyte affinity of magnetic, inorganic nanostructured sorbents for heavy metal contaminants. These new materials contain iron and manganese binding sites that can dramatically impact performance of the material as a sorbent. In addition, the Mn-doping process causes an increase in the specific area through an as yet undetermined mechanism. The enhanced performance of these materials could be attributed to the surface area increase in addition to the change in the chemical specificity. In addition, the Mn-doped materials were tested to determine their heavy metal binding affinity and found to be excellent sorbents.

The Mn-doped iron oxide nanoparticle sorbents have a remarkably high affinity and surface area compared with the precursor material as a result of the oxidative doping technique employed. Sorbent affinity can be tuned toward an analyte of interest simply by adjustment of the dopant quantity. The results show that following the Mn doping process, there is a large increase in affinity and capacity for heavy metals (i.e., Co, Ni, Zn, As, Ag, Cd, Hg, and Tl). Capacity measurements were carried out for the removal of cadmium from river water and showed significantly higher loading than the relevant commercial sorbents tested for comparison. The reduction in Cd concentration from 100 ppb spiked river water to 1 ppb (less than the EPA drinking water limit of 5 ppb for Cd) was achieved following treatment with the Mn doped iron oxide nanoparticles. The Mn doped iron oxide nanoparticles were able to load ~1 ppm of Cd followed by complete stripping and recovery of the Cd with a mild acid wash. The Cd loading and stripping is shown to be consistent through multiple cycles with no loss of sorbent performance.

The recycling experiments were a significant finding due to the inherent instability of organic ligand modified nanoparticles under acidic conditions. The reusability of the Mn-doped sorbent could provide significant cost reduction, and the ability to remove the metal from the sorbent is beneficial when recovery of the metal is desired for applications such as recycling and resource recovery. While some of the experiments performed under this project showed that the addition of reactive surface chemistry (in the form of organic ligands) to these magnetic nanoparticles can greatly enhance their affinity toward some contaminants, the organic ligand modified and polymer coated nanoparticles will not always make good sorbent candidates because repeated exposure to environmental matrices and the chemical regeneration solutions (i.e., acidic solutions) can damage or remove the organic surface coating. Further, organic modification of the surface of the sorbent material adds complexity to the production process and can significantly reduce synthetic yield, increasing sorbent material cost.

Development of Preparative Mass Spectrometry for the Creation of Novel Catalyst Materials

Grant E. Johnson, Julia Laskin

◆ Employed to increase the efficiency of chemical reactions, catalysts are produced predominantly through techniques that do not provide precise control over the size and shape of the resulting materials. This project will employ ion soft landing and *in situ* characterization to prepare size and shape selected depositions of catalytic materials and establish structure-reactivity relationships that will enable the design of next generation catalyst materials. ◆

The structure of clusters and complex molecules on surfaces significantly impacts chemical and physical properties. The current approach to creating shape-selected particles employs solution-phase reduction synthesis. While these methods can produce nanoscale particles with controlled size and morphology, they are unable to access the subnanometer size regime with monodisperse precision. Soft landing of mass-selected ions is a viable alternative approach to the preparation and modification of surfaces and enables unprecedented control over the composition of the resulting materials. For instance, through mass-selected deposition of clusters, species with specific sizes (8–10 atoms) can exhibit pronounced catalytic activity toward reactions such as CO to CO_2 oxidation and propane dehydrogenation. Additionally, electrospray ionization of molecular precursors enables high intensity production of catalytically active ionic clusters for subsequent soft landing onto substrates. Non-thermal ionization techniques such as laser vaporization and magnetron sputtering combined with gas aggregation may also be used to prepare materials that cannot be synthesized easily in solution.

The size and charge state of small metal clusters is known to exhibit a dramatic influence on their optical, electronic, and reactive properties. Using both *in situ* time of flight (TOF) and Fourier transform ion cyclotron resonance (FT-ICR) secondary ion mass spectrometry (SIMS), triply charged gold clusters retain their charge when deposited onto fluorinated monolayers. In contrast, partial and complete charge neutralization is observed when the clusters are soft landed onto carboxylic acid terminated and alkyl thiol monolayers, respectively. These results demonstrate a significant step forward in the ability to control the size and charge state of small metal clusters immobilized on surfaces and will be the subject of a forthcoming publication.

Characterization of the size-dependent structural properties of small clusters relies on clean homogeneous samples for analysis by transmission electron microscopy (TEM). Atomically monodisperse gold clusters were prepared on surfaces and characterized using scanning TEM. The soft landing approach offers unprecedented sample cleanliness as molecular precursors, reactive intermediates, neutral clusters, and solvent molecules are removed and only clusters of a selected size are deposited on the surface. The approach has widespread potential application for the preparation of TEM samples, as it may be extended easily to other materials. These results will also be the subject of a forthcoming publication. Further, metal salen complexes, which are used as olefin epoxidation catalysts, were deposited along with proton donor complexes onto fluorinated monolayers to examine the possibility of achieving proton mediated reactivity in a monolayer. Proton mediated loss of oxygen from $VO(salen)^+$ to form $V(salen)^+$ was observed by *in-situ* TOF-SIMS. Moreover, the original $VO(salen)^+$ complex was regenerated by exposure to O_2. A cyclical pattern of oxidation and reduction was observed providing evidence of catalytic behavior. These results appear in *Physical Chemistry Chemical Physics*.

Ruthenium bipyridine complexes, which are used as chromophores for water oxidation catalysis and catalysts for the water-gas shift reaction, were soft and reactively landed onto a variety of different self-assembled monolayer surfaces (SAMs). It was found that carboxylic acid terminated SAMs bind the complex strongly and that the extent of reactive landing can be greatly enhanced by removing one bipyridine ligand in the gas-phase through collision induced dissociation. The immobilized complexes showed behavior consistent with catalytic activity when exposed to O_2 and C_2H_4. These results were published in *Chemistry – A European Journal*. Also, a new ion deposition apparatus has been constructed and coupled to a commercial TOF-SIMS instrument to enable *in situ* analysis of surfaces prepared by soft- and reactive landing of mass-selected ions. The TOF-SIMS analysis technique has been validated by comparison to results obtained previously by FT-ICR-SIMS. TOF-SIMS exhibits less fragmentation, greater dynamic range, and higher sensitivity than FT-ICR-SIMS, allowing catalytic intermediates with low abundance to be easily detected, as we showed in *Analytical Chemistry*.

Continuing areas of inquiry will include the following: 1) immobilization of solution-phase homogeneous catalysts on substrates and investigation of their reduction-oxidation properties, 2) preparation of atomically monodisperse clusters on surfaces and examination of their size and shape-dependant reactivity, 3) investigation of the charge retention and neutralization behavior of multiply charged metal clusters on surfaces, and 4) structural characterization of subnanometer metal clusters in the gas phase and on surfaces.

Fundamentals of Carbonate Formation: Interactions of Carbon Dioxide with Supported Metal Oxide Clusters

Xiao Lin, Bruce D. Kay, Zdenek Dohnálek

◆ The goal of this project is to obtain a detailed, integrated understanding of how to control catalytic reactions of CO_2 (and relevant molecules) on different oxide catalysts. ◆

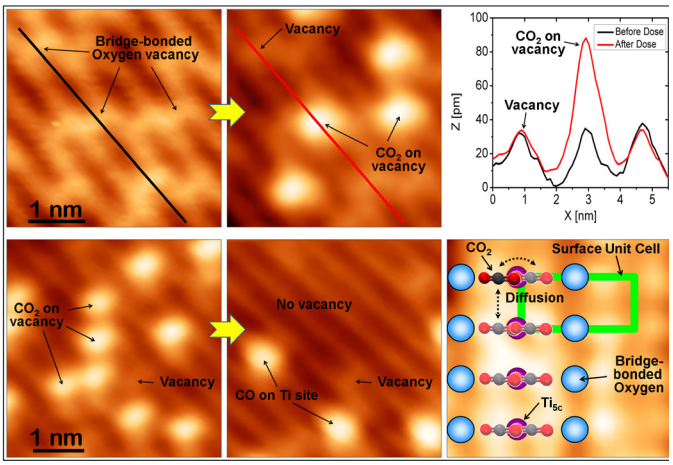
As industries rely on fossil fuel energy and the global warming problem mounts, there is an immediate need to improve our understanding of CO_2 activation, which is instrumental for carbon sequestration and CO_2 fuel conversion. CO_2 adsorption and reactions leading to intermediate species knowledge assists with understanding CO_2 chemistry. We are studying the fundamental aspects of CO_2 adsorption and reactions leading to CO_3^{2-} formation on well-characterized surfaces and supported nanoclusters of model oxides. We are using established methodologies to prepare model surfaces of oxide single crystals (e.g., TiO_2 (110)) and epitaxial films (e.g., MgO(100), Ni(100), CeO_2 (111)). Using novel methods pioneered in our laboratory will create well-defined oxide nanoclusters ranging from fundamental molecular building blocks to larger, variable size nanoclusters. The effect of structure and cluster size on the reactivity of well-defined nanoclusters toward CO and CO_2 will also be explored.

Initially, we focused on relevant molecule interaction with metal oxides surfaces. Previously, titanium dioxide (TiO_2) attracted widespread attention due to its unique properties in heterogeneous catalysis and photocatalysis and potential application in air purification, wastewater treatment, self-cleaning glass, and solar cells. As a part of catalytic carbon cycle, the interaction of alcohols with TiO_2 is studied to ascertain the nature of reactive sites (vacancies and other defects on oxide surfaces) and is expected as a model system to organic contaminant oxidation.

In FY 2010, we studied the adsorption, dissociation, rotation, diffusion, and dehydration of propane-1,3-diol on TiO_2(110) surfaces. Using scanning tunneling microscopy (STM), we found that the diol preferentially binds in bridge-bonded oxygen vacancies (V_Os) via one O-H bond scission, and dissociated diol species rotate around the anchor (-O-CH_2-). At high temperature, diol species on TiO_2 surface dehydrate to form -O-CH_2-CH=CH_2 species and desorb at higher temperature, which is confirmed by temperature programmed desorption (TPD) study.

FY 2011 studies focused on CO_2 molecule interactions with TiO_2(110) surfaces, investigating details CO_2 adsorption, activation, and reaction with TiO_2(110). STM images of TiO_2(110) obtained before and after small *in-situ* doses of CO_2 at ~50 K reveal that CO_2 molecules preferentially bind in V_Os. This behavior is consistent with the observation of TPD experiments. There, a higher temperature desorption peak corresponds to CO_2 molecules bonded on oxygen vacancies with higher adsorption energy. As shown in lower left and middle images of the figure, higher energy (~3eV) electron injection from the STM tip induces CO_2 reduction to CO and oxygen vacancy annihilation ($CO_2 + V_O \rightarrow CO$). This is likely due to the external energy and charge provided by the injected electron. Similar results are obtained using an external source, where higher electron energies (~100 eV) can be achieved.

At higher coverages, CO_2 molecules preferably adsorb on five-fold coordinated Ti sites, where they remain mobile even at 50 K. STM images show a time average of CO_2 binding configurations on Ti rows. Theoretical calculations show that the CO_2 molecules bonded at the Ti sites adopt configurations tilted toward O_b rows and have a low energy barrier for CO_2 diffusion along Ti rows. At coverages close to one monolayer (all Ti sites saturated), the diffusion of CO_2 along the Ti row is hindered, and CO_2 molecules form a stable zig-zag arrangement with 2×2 periodicity. We also studied CO_2 interaction with molecular H_2O (or hydroxyl group) on TiO_2 surfaces. However, STM experiments did not show any substantial interactions of CO_2 with hydroxyl group and/or molecular H_2O, even at ~50 K.



Upper panel: STM images of TiO_2(110) before (left) and after (middle) CO_2 dose, respectively; and STM line profiles (right) as lines in STM images. Lower panel: STM images before (left) and after (middle) high-bias-scan, respectively; and time average appearance of CO_2 molecule (right) diffusing along the five-fold coordinated Ti row.

Future studies will focus on CO_2 interactions with oxygen adatoms on TiO_2(110) and the TiO_2(110) promoted by alkali metal adsorption. We will also study other oxides surfaces (e.g., CeO_2(111)) and oxides clusters. The targeted research will broaden our general understanding of CO_2 chemistry on oxide surfaces.

High Precision Isotope Forensics via Multi-Collector Inductively Coupled Plasma Mass Spectrometry

Garret L. Hart, Douglas C. Duckworth, Benjamin E. Naes, Gary A. Gill, Key-Young Choe, Helen W. Kreuzer, James J. Moran, Bobbie-Jo M. Webb-Robertson, Paul H. Humble, Richard M. Williams, James P. McKinley, Micah D. Miller, Juan Liu, Mark E. Bowden, Kristin H. Jarman, Rachael M. Kaluzny, Janet M. Cloutier

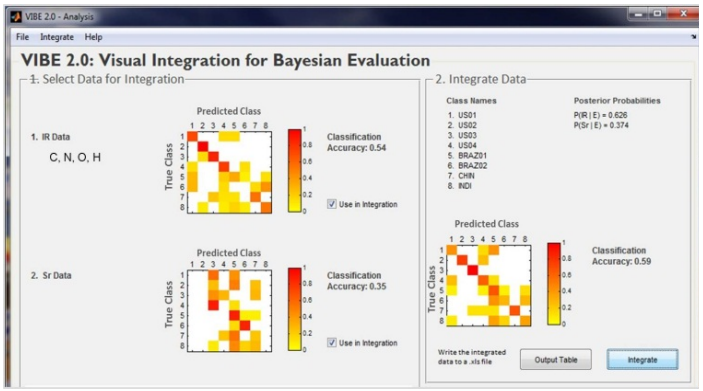
◆ This project strengthens PNNL's contribution to national security by enhancing our recognized excellence in ultra-trace isotopic analysis and extending our capabilities into new areas of high-precision isotopic analysis using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), specifically nuclear material characterization and material analysis using radiogenic isotope systems. ◆

The scientific basis and application of nuclear isotope ratio measurements is well-known within PNNL. The application of radiogenic isotopes in geochemical (and more recently forensic) studies is also well documented and is a complementary technique to stable light isotope analysis for forensic applications. Radiogenic isotopes such as Sr and Pb are known to vary substantially in nature based on primordial elemental parent-daughter crustal abundances of the locale and therefore retain a regional signature preserved in mineral laden dust and metal ores.

The goal of this project was to evaluate the efficacy of special nuclear material analyses via in-torch thermal vaporization (ITV), to develop the use of radiogenic isotope ratio information for provenance determination of dust, and to isotopically characterize highly-refined metals. These efforts required development of chemical and analytical protocols for the MC-ICP-MS on a variety of substrates for isotopics that could be utilized for provenance characterization. During the course of our work, several substrates were successfully prepared and tested.

In-torch vaporization – uranium analysis. The unique features of thermal ionization techniques were coupled with the advantages of a state-of-the-art MC-ICP-MS. Such an approach benefits from minimal sample preparation while retaining the rapid through-put of ICP-MS instrumentation. The unique ICP-MS multi-collector array allows simultaneous measurements of all uranium isotopes on detectors ideally suited for the expected beam intensity for U isotopes. The ICPMS also has very high sample utilization efficiency (SUE) for a dry plasma source due to an enhanced sample introduction interface and vacuum pumps. We focused our efforts on both liquid and solid uranium standards loaded on to Tantalum filaments. A miniaturized electro-thermal vaporization apparatus was created for rapid, efficient analysis of solids and liquids. Calculated sample utilization efficiencies were equivalent to laser ablation techniques (liquid = 0.17%; solid = 0.03%), but sample throughput was 40-50 samples/day.

Provenance determination and sample characterization: strontium and lead isotopic ratios in diverse matrices. Sample provenance – where samples originated – is of great interest to many different groups. Such information can be determined through careful physical, chemical, and isotopic characterization of a sample that generates a multi-dimensional data set. These data sets can then be subjected to advanced data analysis that yields predictive provenance probabilities. In this project, our efforts focused on the ability to generate data sets (particularly isotopic data) from a variety of different matrices, including castor beans, dust and water samples, human hair, and copper metal. For each of these matrices, a separation protocol was developed that was tailored to the specific challenges of that matrix. A method was developed that uses a chelating adsorption resin specific for isolating Pb and Sr in a mixed matrix of HNO_3/H_2O_2, assisted with a heated block digester. High precision isotopic analyses where then obtained, which were then evaluated through Bayesian statistical approach.



Advanced data analytics: A screenshot of the classification accuracy plots associated with an average probability model across 1000 iterations shows how many misclassifications within individual datasets are corrected in the integrated model.

We have demonstrated the capability to generate high-quality isotope ratio data from a wide spectrum of sample matrices on a multi-collector ICPMS. We have developed novel techniques and protocols specific to sample type that aid in sample utilization and throughput. These isotopic data can be combined with other data through advanced data analytics to predict where a sample did or did not come from.

In Situ Molecular-Scale Investigations of Reactions between Supercritical CO_2 and Minerals Relevant to Geological Carbon Storage

John S. Loring, Zheming Wang, Christopher J. Thompson, Jian Zhi Hu, David W. Hoyt, A. Scott Lea, H. Todd Schaef, Kevin M. Rosso

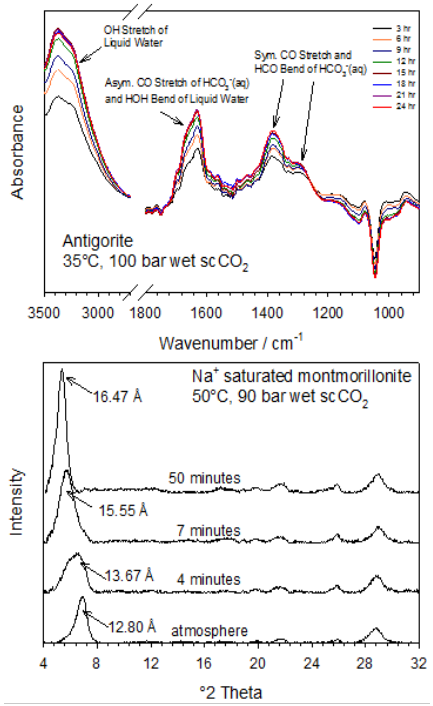
◆ This project will result in new, unique data for molecular mineral transformation processes involved in carbon capture and sequestration, including processes from mineral dissolution/nucleation/precipitation and hydration/dehydration to in situ sorption/desorption studies in supercritical carbon dioxide ($scCO_2$). ◆

Geologic carbon sequestration (GCS) is an important strategy being implemented to slow the flux of carbon dioxide emissions from the burning of fossil fuels. This technology involves injection of CO_2 deep underground, for example in saline basalt formations or exhausted oil wells. At injection depths, this greenhouse gas will exist as a supercritical fluid. In the near term, buoyant $scCO_2$ plumes containing variable water concentrations could displace aqueous solution and dominate the pore space adjacent to injection well bores and caprocks. To predict the viability and risks of GCS, it is vital that we understand the reactions at reservoir conditions between wet $scCO_2$ and host and caprock minerals.

The purpose of this project is to gather and interpret in situ experimental data on the reactions of $scCO_2$ containing variable concentrations of water with a range of geologically relevant host and caprock materials, including clays, olivines, serpentines, chlorites, feldspars, and rock core samples. This project's success will lead to an increased understanding of geologically relevant mineral transformation processes in low water $scCO_2$, which will help to inform and guide development of reactive transport simulations tailored for subsurface CO_2 reservoirs.

Starting with FY 2009, a suite of experimental capabilities at PNNL was developed to investigate reactions at high-pressures and moderate temperatures between minerals and $scCO_2$ containing small amounts of water. Methods included infrared (IR) spectroscopy, magic angle sample spinning nuclear magnetic resonance (NMR) spectroscopy, atomic force microscopy (AFM), and x-ray diffraction (XRD). A key objective of the new approach as well as the chief goal of this project is to understand at a fundamental level the mechanisms and rates of transformation processes of geologically relevant host and caprock minerals exposed to wet $scCO_2$.

With a project start in late FY 2011, the focus has mostly been to finish experiments that were already underway on the olivine, forsterite, and the serpentine, antigorite, and to initiate studies on the clay, Na^+-montmorillonite, and prepare for the mineral studies. Experimental results included data analysis and manuscript preparation for an IR spectroscopic study comparing the reactivity of forsterite and antigorite with wet $scCO_2$ at 35°C and 100 bar, where thin liquid water films containing dissolved Mg^{2+} and bicarbonate were detected, and data collection in an XRD study of the reaction of Na^+ montmorillonite containing one water layer with dry and wet $scCO_2$ at 50°C and 90 bar, where clay expansion or dehydration was shown to occur depending on the water concentration in the $scCO_2$.



Top: In situ IR spectra of antigorite reacted with wet $scCO_2$ as a function of time. Bottom: In situ XRD tracings of Na^+ montmorillonite at atmospheric conditions and as a function of time following pressurization with wet $scCO_2$.

In addition to completing experiments and publishing our results during FY 2012, we will 1) finalize forsterite and preliminary antigorite results; 2) finish integrated IR and HXRD experiments with sodium saturated montmorillonite; 3) initiate and complete an integrated IR, NMR, and HXRD study on antigorite; 4) acquire and characterize clinochlore and anorthite samples; and 5) initiate integrated IR, NMR, and HXRD experiments with clinochlore and anorthite.

Increased Sensitivity and Improved Quantification of TH and U in Particles by SIMS

Albert J. Fahey, Scott C. Szechenyi, Janet M. Cloutier

◆ This research will lead to a basic understanding of how oxide and elemental ions form on various substrates and under different conditions through measurements of elemental oxide and dioxide signals from single particles under prescribed conditions and may yield to an over-determined system amenable to least squares analysis, providing redundancy and consistency checks on the validity of the resultant data. ◆

A specific high-value method involving the measurement of thorium and uranium was developed during the late 1990s. In advancing the method from its current state, the ionization efficiency of elemental and oxide ions will be explored for various substrate materials and under conditions of oxygen flooding. The primary focus of this research is to increase the ion signal intensity of the oxide and dioxide ions of thorium and uranium in secondary ion mass spectrometry (SIMS). Once the magnitude of the effect is measured and confirmed on the PNNL IMS-4f, samples will be investigated on an IMS-1280. Data and methods pertaining to both application of the method and the fundamental mechanisms of sputtering ionization will be obtained and analyzed.

Additionally, this research will address two related issues that arise from our observations. The first issue that is directly applicable to improving measurements for nuclear non-proliferation and forensics, we will determine the optimal protocol for uranium, focusing on ionization the efficiency, identification, and reduction of interferences, increased signal stability, and lower statistical variability. The second issue will focus on understanding the basic mechanism of oxide and ion formation. To this end, other compounds will be characterized on the various substrates used. We will attempt to understand and quantify these results, specifically relating them to basic chemical properties of the element and oxide ions formed.

By the end of FY 2011, initial steps were taken to obtain sample and substrate material and to bring the laboratory up to operational status for this project. Specifically, substrate materials were procured to mount uranium oxide particles with the appropriate doped trace elements. A cursory method was developed to produce substrates for SIMS for silicon and gold materials. Additionally, purchased polished graphite substrates were also used. Finder-grids were evaporated on the silicon and carbon substrates through an etched Mo mask to facilitate the relocation of particles once dispersions were made. Initial results were obtained.

Initial experiments were performed after synthesizing new materials, producing appropriate substrates and bringing the instrument to operation status. Sample material was not available through previously arranged channels, so alternatives were explored at PNNL. A staff member at PNNL was identified as being able to synthesize the appropriate materials. Two materials sets were synthesized and analyzed for preliminary concentrations of thorium and uranium by gamma spectrometry. Sample mounts were made by dispersing the materials on carbon, silicon, and gold substrates. Initial data was acquired by SIMS under conditions of oxygen flooding at 10^{-6} torr and under high vacuum (10^{-8} torr). Enhancements were achieved of approximately a factor of 30 for these initial measurements. These significant enhancements were shown to be achievable with the appropriate choice of substrate and oxygen-surface-flooding conditions.

Follow-up experiments will be performed to provide absolute efficiency enhancements for the signal increases. This will involve SEM work to locate and re-locate particles of interest on each substrate. Linearity and interference contributions will be investigated and final trial runs will be performed at a secondary laboratory on the IMS-1280. More specifically, we will be working in FY 2012 with choosing thorium and uranium particles and characterizing sizes in the SEM on three different substrates, which will require mapping positions for later re-location in the IMS-4f. Also for the IMS-4f, we will make measurement comparisons to extinction on three selected substrates (e.g., C, Si, and Au) and determine the relative enhancement factors. Further, we will perform additional measurements to characterize the in-measurement variability of the ion signals and ratios. We will conclude by comparing the ultimate sensitivity between elemental and oxide ion methods.

Light Source Photocathode Performance and Development

Wayne P. Hess, Theva Thevuthasan, Scott A. Chambers

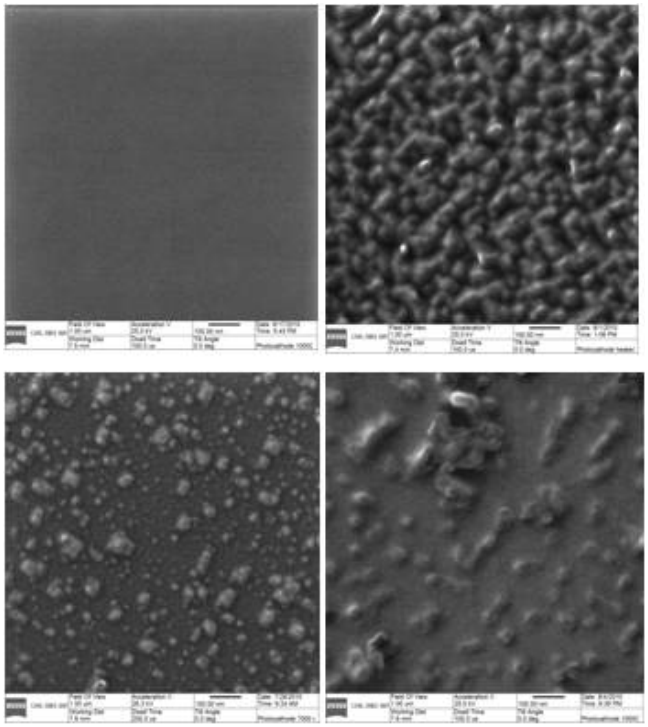
◆ This project will develop new research capabilities for developing and testing existing photocathode materials and designs. We will develop methods for measuring photophysical properties including work function, photon energy dependent electron yield (bunch intensity), and emittance (electron angular distribution). ◆

Whether based on free electron laser (FEL) or storage ring designs, output characteristics and cost of new ultraviolet or x-ray sources are dependent on photocathode brightness and emittance characteristics. Novel photocathode designs could potentially reduce light source construction costs enormously—by a factor of two or more—by significantly simplifying downstream accelerator or FEL design. The international light source community recognizes the need for a more scientific approach to new photocathode development and is in initial stages of addressing this issue; however, no consensus exists within the user community for the mechanisms of photocathode damage.

This project will develop new capabilities for making and testing photocathode materials and enhancing photocathode designs to improve current and future light sources in a collaborative effort. Our Initial goals are to increase photocathode longevity by understanding and modeling photocathode failure mechanisms. We will conduct post-mortem analysis of used (expired) photocathodes from the Thomas Jefferson National Accelerator Facility Laboratory to determine how photocathode emission yield degrades under operating photo-injector conditions. For this testing, we will interrogate various photocathode types with x-ray photoelectron spectroscopy (XPS), two-photon photoemission (TPPE), and angle resolved photoemission spectroscopy (ARPES). To make and test potential photocathode materials requires construction of a materials growth chamber that is vacuum-coupled to an existing photoelectron spectrometer.

In FY 2010, we commenced with our post-mortem analysis of expired photocathodes, which yielded a manuscript detailing the results to a journal. Our helium ion and atomic force microscopy images revealed that the photocathode activation procedure leads to dramatic roughening of the photocathode surface – a surprising result that dramatically impacts the electron emittance. Highly detailed Rutherford back scattering spectrometry (RBS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) results were obtained. The RBS results showed the photocathode lattice to be highly crystalline despite the surface roughening with no indication of bulk damage due to ion backscattering in the FEL photoinjector chamber. The TOF-SIMS results indicated no ion implantation and light surface contamination, consistent with that introduced during sample handling under relatively clean conditions. Stoichiometry analysis by atom probe tomography (APT) and XPS indicates possible Ga enrichment in the near surface region. We also determined the Cs surface distribution which is consistent with records of re-activation cycles during FEL operation.

We developed several tools during our FY 2011 endeavors. A multi-source thin film deposition chamber was constructed, including installation and testing of three effusive ovens for chemical vapor deposition and vacuum sample transfer. This design allows for the in-situ growth of coated photocathodes for interrogation by XPS, TPPE, and ARPES. We tested the deposition chamber by coating a silver substrate with two monolayers of MgO and performing XPS and ultraviolet photoelectron spectroscopy (UPS). The XPS results showed the oxide film to be radiation resistant, while the UPS results confirmed the predicted reduction in work function from 4.3 to 3.0 eV.



The panels are 1 μm field of view helium ion microscope images of photocathode surfaces as the GaAs wafer is progressively conditioned and undergoes operation. Upper left: smooth surface of an unused wafer; upper right: first conditioning step of heating the wafer and adding a Cs monolayer, which results in surface roughening; lower panels: changes to surface morphology after the wafer has generated 1000 and 7000 Cs emission, respectively.

We further modified the photoelectron spectrometer to characterize photocathode properties, including a photon energy dependent electron yield (bunch intensity) and emittance (electron angular distribution).

In FY 2012, we will produce a clean single-crystal Ag(100) surface, with and without a two monolayer MgO film, and measure the work function, angle resolved UPS, and normal emission XPS of each. We will produce a CsBr:Cu photocathode and characterize mid-gap states using laser excitation at 4.7, 6.4 and 7.9 eV. We will then anneal sample to test importance of F-centers in emission mechanism. We will activate a Cs:GaAs photocathode without high temperature heat treatment and characterize the photoelectron emittance and surface morphology using helium ion microscopy and scanning probe microscopy, as needed. We will image photoemission from either a CsBr:Cu or Ag(001):MgO photocathode using photoemission electron microscopy.

Methodology and Tool Development for Rapid Assessments for CO_2 Capture Technologies

Charles J. Freeman, Mark D. Bearden, Paul H. Humble, Greg A. Whyatt, Daryl B. Brown

◆ This project has developed a research methodology for evaluating novel CO_2 capture technologies, which requires a blend of experimental, thermodynamics, chemical process engineering, flow sheet modeling, and economic forecasting. The methodology allows for guiding investments in future carbon capture technologies being considered by PNNL. ◆

Commercial CO_2 capture technologies exist, but at much smaller scales than what will be required for global CO_2 reduction targets. Existing technologies have forecasted coal power plant output efficiency reductions of nearly 30%, which makes justifying their implementation difficult, if not impossible. A large number of energy efficient CO_2 capture technologies have been proposed by a wide body of organizations to address the implementation barrier. Concepts range from conventional liquid and solid sorbent separations, to cryogenics, oxygen combustion, and chemical looping. Technology leaders in the gas separations area, including groups within DOE, are now struggling to determine the most promising directions to reach the desired goal. Further, as investments occur in a greater number of different technologies, overall development costs increase.

This project focused on developing a methodology that allows for rapidly assessing and down-selecting carbon capture technologies at various levels of maturity. The methodology is based on the Technology Readiness Level (TRL) scale established by NASA. Along with decision gates, we used this scale to develop an overall architecture for methodically progressing technology candidates. We have coined this as the "TRL-Gate Methodology." The project focus has been on determining the minimum amount of analytical/experimental measurements required to complete thermodynamic and engineering assessments to determine if key performance thresholds are met at each technology TRL gate. Our estimates show that the development costs for all current DOE and industry carbon capture investments could be reduced in half by improving the down selection of technologies at the two earliest stages of technology development, which would also translate into schedule acceleration for the remaining technologies.

We completed an initial framework of the proposed methodology for both solvents and sorbents in FY 2010. Several gate assessments of the PNNL sorbents were made throughout the year, though some experimental data was inadequate. We then focused our efforts on several tasks, including full plant solid sorbent assessment, initial assessment of cryogenic flue gas cleaning, novel compression concept for physical sorbent concept, integrated plant assessment for catalyzed potassium carbonate, and assessments of multiple carbon capture technologies.

For FY 2011, we continued to test and refine the methodology and experimental requirements with significant input from industry. We were able to establish a key working relationship with experts at the Fluor Corporation, who helped

TRL 2 Gate Assessment Criteria:	MEA	13X	MOF	NanoZ	Chitosan	K2CO3	CO2BOLs	CO2BOLs / PSAR	Chilled NH3
Separation and Compression of CO2:									
Heat of Reaction for CO2 (kJ/kg CO2)	1,578	639	876	686	4,480	780	1,534	1,534	1,384
Adsorber Temperature (C)	40	40	40	40	40	40	40	40	5
Sorbed CO2 / Sorbed N2 (absorber conditions)		27	23	10					
Desorber Temperature (C)	120	80	100	60	60	60	90	60	70
Sorbent Regeneration Rate (kg/ kg CO2 removed)	32	42	30	105	473	118	41	41	14
Thermal Energy - no compression (kJ/ kg CO2)	3,648	1,237	1,533	1,414	7,713	2,850	1,906	1,744	1,909
Work Required from Plant Steam Cycle (kJ/kg CO2)	1,193	783	706	907	2,228	1,207	747	658	916
Minimum Lost Work (kJ/kg CO2)	835	578	506	616	640	620	466	299	562
Flue Gas Dehydration via TEG (if required):									
Sorbed CO2/ Sorbed H2O (absorber conditions)		0.4	0.4	0.8					
Dehydration Required?	No	Yes	Yes	Yes	No	No	No	No	No
Work Required from Plant Steam Cycle (kJ/kg CO2)		294	294	294					
Minimum Lost Work (kJ/kg CO2)		259	259	259					
Totals (Separation, Compression and Dehydration):									
Work Required from Plant Steam Cycle (kJ/kg CO2)	1,193	1,077	999	1,201	2,228	1,207	747	658	916
Minimum Lost Work (kJ/kg CO2)	835	837	765	875	640	620	466	299	562

Energy penalty estimates for carbon capture sorbents and solvents using PNNL's TRL-2 Gate Methodology.

identify significant enhancements to our methodology. This led to a body of analyses that could not be performed with PNNL equipment and had to be outsourced (working with high pressure, H_2S-containing gases). The results have allowed us to predict the gas separation and corresponding energy penalties.

Most of the data collection and analysis efforts this year was on the first two gates, TRL 2 and TRL 3. We focused our analyses on four solid sorbent materials (three developed at PNNL) and five solvents (one developed at PNNL). Optimum energy estimates were made for each solvent and sorbent based on the isotherms and vapor-liquid equilibrium data collected as part of TRL Gate 2. Energy optima were based on combinations of both regeneration temperature and pressure, and required quantification of reaction, sensible and vaporization energies. Monoethanolamine (MEA) was quantified as a baseline comparison. The results of the TRL Gate 2 comparison showed that only three of the eight technologies passed the energy criteria (a reduction in energy of 25% or more compared with MEA had to be shown). However, five out of eight passed this criterion from a "minimum lost work" basis, which means that advanced heat integration schemes could enable those options. The leading solid sorbent options all suffered from quantified water uptake issues, resulting energy penalty. However, if these sorbents could be tailored to improve selectivity of CO_2 over water, they could pass the TRL 2 Gate criteria (as evidence from their pre-dehydration energy projections).

A key outcome of the TRL 2 gate analyses is the minimum lost work opportunities. As discussed, these estimates unveil options for regenerating a solvent or sorbet without having to access the primary steam cycle in a given power plant. For the PNNL-developed CO_2BOLs, the minimum lost work predictions were substantially lower than the current MEA baseline. This was improved even more by the incorporation of polarity-swing assisted regeneration (PSAR). The result was a the conception of a novel heat pump arrangement for the CO_2BOLs/PSAR technology.

Now that the experimental and assessment tools have been developed, the above experimental/analysis can be performed for less than $100K for most materials. This cost is far less than many companies and DOE current investment in carbon capture technologies before any significant go-no go decisions are made.

Assuming that a technology passes through the TRL 2 Gate, the next step is the analyses and engineering estimates associated with the TRL 3 Gate. There, the assessments are largely based on kinetic measurements of the system. This fiscal year represented the first real PNNL measurements of kinetic behavior CO_2 capture solvent and sorbents. We relied heavily on the LDRD equipment investments in wetted-wall and solid sorbent breakthrough testing. This year, kinetic measurements were made with K_2CO_3, MEA, MDEA, and CO_2BOLs solvents. The results showed that K_2CO_3 kinetics were approximately $1/10^{th}$ of MEA, which would require relative commercial absorber towers more than 10x in height. This result supports the need for a catalyst in the K_2CO_3 system, which aligns with current DOE investments in enzyme technology. CO_2BOLs kinetic measurements were actually higher than the MEA baseline, enabling its successful pass through the TRL 3 Gate.

Another key accomplishment this fiscal year was a detailed analysis of the leading compression/cryogenic concept for carbon capture. This involved direct engagement with Sustainable Energy Solutions, the owner of that technology.

At this project's end, much of the developed capability is being rolled into other programs. An important target for the capability is DOE's new Carbon Capture Simulation Initiative (CCSI), which involves five national laboratories (including PNNL) and is focused on accelerating carbon capture development through advanced simulation.

Molecular Structure and Interaction at Aqueous, Non-Aqueous Liquid Interfaces and Catalytic Solid Surfaces

Hongfei Wang

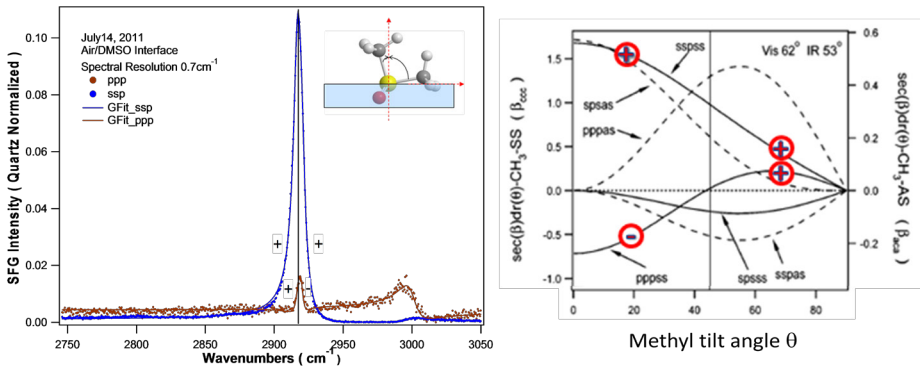
◆ Using cutting-edge instrumentation, this project will lead to new discoveries in surface science and have broad applications on the characterization of structure and interactions at various molecular interfaces that are critical but elusive in many scientific and engineering fields. ◆

The interface selectivity and submonolayer sensitivity of the second order nonlinear optical spectroscopy make it a unique tool to study the structure and interaction of molecules at various surfaces and interfaces relevant to energy as well as environmental and biological processes. In the second order optical method, two photons with the same frequency (second harmonic generation) or different frequencies (sum-frequency generation) interact simultaneously with the same set of atoms or molecules to generate a new photon at the sum of the frequencies. The symmetry requirement for these processes forbids the processes from the bulk liquid or amorphous solid with centrosymmetry but allows them to be generated from the surface or interfaces that always have asymmetry. The new photon generated is also background free from the large number of incoming photons, so it allows sensitive detection such as photon counting for submonolayer level vibrational and electronic spectral measurement.

For the past two decades, scientists have been using this tool to understand and characterize the details of the structure and interactions at various molecular surfaces and interfaces. PNNL played leading roles in developing the experimental methodology and theoretical treatment to push forward the advancement in this field from the simplest air/liquid interface to more complex liquid/solid, liquid/liquid, liquid/membrane, and nanoparticle interfaces. This has been a growing field and is ready for exploring applications related to molecular and biological surfaces and interfaces.

This project aims to employ the recent development of ultrafast laser technology to push the surface nonlinear spectroscopy and dynamics unprecedentedly to higher spectral resolution, time resolution, and detection sensitivity to solve problems with complex molecular surfaces and interfaces. It is a unique capability that will positively impact in understanding molecular surface science, especially to complex surfaces that ubiquitously exist in energy, environmental, and biological systems that cannot be accessed or studied in situ and at ambient or extreme conditions using other x-ray, electron, or ion probe tools and instrumentations.

This project commenced in 2010 to support experimental and theoretical studies applicable to various aqueous, non-aqueous liquid interfaces and catalytic solid surfaces. We developed and employed the unique surface nonlinear spectroscopy and dynamics capabilities using state-of-the-art ultrafast lasers together with the quantitative methodology in nonlinear spectroscopy and dynamics to investigate important interfacial problems in the energy, environmental, and biological heterogeneous and homogeneous chemical processes. The key to successful completion rests on the successful design, construction, and testing of the complete laser system; the nonlinear optical experimental setup; and the various optical cells to be used for various surface measurements. All design and construction were underway, setup, and tested by the end of the year.



The HR-BR-SFG spectrometer enables measurement with unprecedentedly accurate line shapes in different polarization combinations. For the air/ dimethyl sulfoxide (DMSO), line shapes in different polarization combinations enable resolving the peaks of the two methyl groups of the interfacial DMSO molecule, which appear to be one peak in each spectrum in the ssp and ppp polarization combinations, respectively. The actual separation between peaks is 2.5 cm^{-1}, compared with full width at half maximum ~8-9 cm^{-1}. In addition, the phases and oscillator strengths of the ssp and ppp spectra can accurately determine the tilt angle from the interface normal of the two methyl groups. Such information has not been expected to be obtained, but this development is expected to change the related field of studies significantly.

In FY 2011, we successfully built the world's first high resolution broadband surface sum-frequency generation vibrational spectrometer (HR-BR-SFG-VS). Spectral resolution is ~0.5-0.7cm^{-1}, about 10 to 20 times better than current BR-SFG spectrometers. High resolution SFG-VS spectra allow accurate measurement of the surface SFG

spectral line shape, allowing spectral line shape analysis and detailed SFG spectral phase analysis through accurate SFG intensity spectra measurement. The ability for surface SFG-VS to resolve detailed chemical shifts and structure of the molecular interface shall make SFG-VS a unique analytical tool. For non-aqueous liquid and solid/liquid interfaces using high resolution and scanning SFG-VS spectrometer, we observed catalytic reaction product of from acetic acid on CeO_2 nanoparticle surface, with the established procedure for using SFG-VS in in situ nanoparticle surface characterization; measured and analyzed the hydrogen bonded water spectra at the aqueous/SiO_2 and aqueous/CaF_2 surfaces; and measured the surface keto-enol structures of acetylacetone, a model ligand in liquid-liquid extraction of heavy elements under different conditions.

In 2011, we showed that the high resolution and excellent line shape in HR-BB-SFG-VS enables resolving spectral and structural details of molecular interface, which was not attainable before. During FY 2012, we will continue the research on various molecular interfaces focusing on the two following aspects: 1) pushing the limit for resolving spectral and structure details of relatively simple liquid surfaces, and 2) applying what have been learned to study the spectral and structure details of complex and inhomogeneous surfaces and interfaces, such as nanoparticle surfaces, aqueous/oxides interfaces, and catalyst surfaces. We will also try ultrafast dynamics measurement with SFG-VS, starting with the vibrational free induced decay. These studies shall significantly move the field of surface nonlinear spectroscopy forward. This will lead the project not only to a deeper fundamental understanding of the molecular interface but also – and more importantly – provide new tools and open opportunities in surface/interface studies.

Multiscale Investigation of CO_2 Behavior in Subsurface Under Extreme Conditions

Alexandre M. Tartakovsky, Bruce J. Palmer, Uditha C. Bandara

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

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

Given these challenges, we are developing a multiscale modeling approach to simulate CO_2 behavior (flow and precipitation) in the caprock at the pore and sub-pore scales. This approach uses kinetic Monte Carlo (KMC) model coupled with diffusion equation to study surface precipitation dissolution reaction and smoothed particle hydrodynamics (SPH) model of pore-scale flow and reactive transport. KMC models alone cannot cover all the length and time scales necessary and relevant to understanding the fundamental processes involved in CO_2 sequestration. The hybrid model will bridge the molecular and pore-scale models of the CO_2 behavior in subsurface. In addition, the hybrid model will serve as a basis for upscaling CO_2 behavior from fundamental scales to scales of practical importance.

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

In FY 2011, we developed a pore-scale SPH multiphase flow model that studies different trapping mechanism of supercritical CO_2 in subsurface reservoirs. The model is implemented as a part of a general purpose high performance SPH code. The scalability of the code was tested on PNNL's Chinook supercomputer. A good scaling performance was observed for up to 1000 CPUs. A Darcy scale fully Lagrangian particle model for flow and transport was developed and used to simulate gravity driven unstable flow of fluids with different densities. This model has been used to investigate the downward migration of dissolved CO_2. The preliminary numerical simulations of micro-fluidic, two-fluid experiments were performed. We also developed a novel dimension reduction method for large ODE systems that can significantly accelerate pore-scale simulations regardless of the nature of a numerical solver. The method relies on a computational closure, achieved via short bursts of a pore-scale model conducted in small portions of the computational domain of averaged evolution balance equations. The dimension reduction model was used to simulate flow and transport with mixing controlled reactions and mineral precipitation. The good agreement with micro-fluidic experiments confirms the accuracy and computational efficiency of the dimension reduction model. Four papers summarizing this research were published in peer-reviewed journals.

The goal of the developed multiscale models is to simulate flow and reactive transport on a laboratory scale and/or the scale of a representative elementary volume. The model can also be used to guide and interpret laboratory experiments and create a database for use with advanced reservoir simulators. The multiscale model creates a unique capability for understanding complex geochemical interactions of heterogeneous subsurface environment with fluid mixtures.

Multiscale Modeling from Molecular Reactions to Catalytic Reactors

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

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

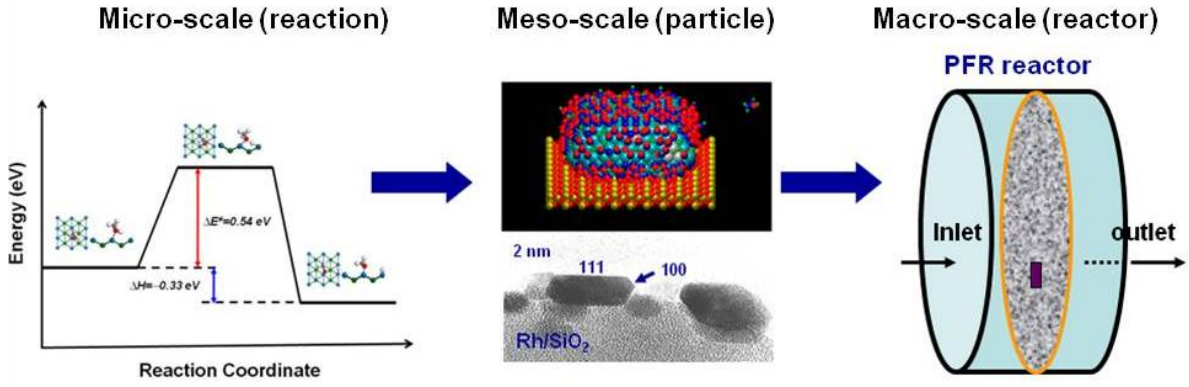
A formidable challenge in catalysis research is understanding the mechanisms and dynamics of molecular transformations over catalyst materials under operating reaction conditions. Molecular-level knowledge about catalytic reactions can enable one to design catalysts with improved efficiency (selectivity, yield, and cost) of targeted products. However, operating conditions in reactors cause inhomogeneous temperature and pressure gradients experienced by the catalyst particles, which dramatically complicates the macroscopic prediction of global kinetics and reaction yields.

We are developing a new module that describes heterogeneous catalytic processes from the quantum chemistry level up to reactor level under practical operating reaction and flow conditions. The most challenging task in this unique computational module is linking the various theories and models at different time and length scales seamlessly and dynamically. We attempted this linkage by modeling a non-uniform flow phase using both kinetic Monte Carlo (KMC) and stochastic partial differential equation (SPDE) methods. The power of the new capabilities is highlighted for specific catalytic systems by elucidating and predicting the catalytic transformations under practical reaction and flow conditions of a reactor.

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

We expanded the KMC model for FY 2010 with a second order grid-based finite-difference. The new, integrated computational framework consisted of a surface phase domain and a gas-phase boundary layer domain imposed on the catalyst surface. At each time step, heat and mass fluxes between two domains were calculated simultaneously until the steady-state reaction condition was reached, during which the activity, surface coverages of reaction intermediates, and temperature and pressure gradient profiles in the gas-phase boundary layer were statistically constant. In addition, we also developed a novel theoretical and numerical model that combines particle simulations and finite-difference partial differential equation (PDE) models applied for reaction diffusion systems at low concentration. Unlike most of existing stochastic and deterministic finite-difference models, instead of deriving from macroscopic PDE and SPDE, our new model is specifically formulated in terms of discrete rather than continuous probability distributions.

During FY 2011, a multiscale computational model that couples first-principles based KMC simulation and a grid-based finite-difference Crank-Nicolson continuum model was developed. The dynamically coupled multiscale model consisted of two phase domains. The surface phase domain is modeled by the site-explicit first-principles KMC simulation. The gas-phase boundary layer domain was described using the second-order Crank-Nicolson method. The temperature and pressure gradients in the gas-phase



Multiscale hierarchy for catalytic reactor model informed from kinetic model and molecular reactivity.

boundary layer are the consequence of thermal and molecular diffusions of reactants and products under nominal reaction conditions. We used the newly developed model to study the effects of heat and mass transfer on the reaction kinetics of CO oxidation over the $RuO_2(110)$ catalysts, as the heat from CO oxidation is allowed to be dissipated only into the gas-phase via thermal diffusion. By varying the particle size (thickness) of $RuO_2(110)$ catalysts, the surface temperature changes correspondingly with the heat produced by occurring surface reactions, as does the surface pressure. Our results indicate that the observed reaction kinetics of CO oxidation on $RuO_2(110)$ catalysts largely depends upon how the reaction heat, the reactants and products being exchanged with the invariant bulk gas-phase far from the surface. Even without including the bulk flow and the gas phase reactions, the heat and mass transfer induced by the size and the heat conductivity properties of a catalyst could dramatically cloud the intrinsic reaction kinetics in the experiments. Our model clearly demonstrates that a reliable model for predicting heterogeneous reaction kinetics need to include the accurate description of heat and mass transfer in the surrounding reaction environment and their effects on the reaction kinetics. This work has been published on the peer-review journal *Catalysis Today*.

Also during FY 2011, we developed a hybrid numerical model that combines KMC for a surface reaction domain and to finite difference model for bulk continuum phase domain. We considered two representative problems that validate a hybrid method and also demonstrated that this method captures the combined effects of nonlinearity and stochasticity. Our results showed that the KMC-continuum hybrid and fully deterministic simulations do not agree. Because KMC captures inherent fluctuations, we consider it to be a more realistic than a purely deterministic model. Therefore, we demonstrated that the KMC-continuum hybrid model is more representative of the catalytic system. This work has been submitted to *Physical Review E* for publication.

In order to capture the small-scale heterogeneity, a new stochastic multiscale method that ensures both local and global mass conservation is being developed as part of this project. Starting from a specified covariance function, the stochastic log-permeability is discretized in the stochastic space using a truncated Karhunen-Loeve expansion with several random variables. The adaptive high-dimensional stochastic model representation technique (HDMR) is used in the stochastic space. HDMR decomposes the high-dimensional problem into a set of low stochastic dimensional subproblems, which are efficiently solved using the adaptive sparse grid collocation method. Numerical examples are presented to show the accuracy and efficiency of the developed stochastic multiscale method. This work will be published on the peer-review journal *Physics of Fluids*. Currently, we are preparing two more papers. In summary, a total of six publications and seven presentations will be the outcomes from this project.

Multiscale Synthetic Studies Targeted Towards the Development of Nanostructured Heterogeneous CO_2 Reduction Catalysts

János Szanyi, Abhijeet J. Karkamkar, Ja Hun Kwak, Roger J. Rousseau, Zdenek Dohnalek

◆ The aim of this work is to synthesize, characterize, and test two families of nanostructured materials with catalytic activity toward CO_2 reduction. ◆

Transition metals have been shown to be active components of homogeneous and heterogeneous catalysts in the conversion of CO_2 to either methanol or methane. Understanding the requirements that govern the activities and selectivities of the catalytic centers in the reduction of CO_2 will enable us to design and synthesize nanostructured, bioinspired heterogenous catalysts operating at moderate temperatures with the desired selectivities. Due to its high thermodynamic stability, CO_2 is the most underutilized carbon source in the production of high energy density organic molecules. To minimize the energy requirement of the chemical conversion of CO_2, heterogeneous catalysts with high production effeiciencies and selectivities are required. To this end, understanding both the elementary steps of the reduction process and the nature of the active catalytic centers (and then the design and synthesis of these atcive centers) are necessary.

Transition metals alone have been proven ineffective for the activation of CO_2 leading to the development of bi/multi-functional catalytic systems. In enzime catalysis, Lewis acid-base pairs are utilized for the activation CO_2 that ultimately leads to its reduction at ambient temperatures. The activation of CO_2 needs to be accompanied by a reduction function of the catalyst, requiring the presence of a transition metal for the activation of molecular hydrogen. These functionalities can conveniently be built into heterogeneous catalysts containing both metals and oxides as active components.

In the course of our research, we will design and construct active sites for CO_2 reduction from two directions: well-defined metal clusters on oxides and multifunctional nano-scale clusters. First, we are designing and synthesizing oxide-supported metal catalysts with a wide range of dispersion: atomically dispersed metals, two-dimensional rafts, and three-dimensional metal clusters. These materials allow us to understand the effects of the metal oxidation state, the role of metal and oxide support interaction, and the importance of the oxide itself in the overall CO_2 reduction activity and product selectivity. Next, multifunctional catalysts utilizing polyhedral siloxane building blocks will be designed synthesized and tested. These supramolecular architectures allow the fine tuning and optimization of the functionalities required for the reduction of CO_2 (e.g., interaction between Lewis acidic metals with soft and hard Lewis bases). The primary project goal for both subtasks this year (project started mid-year FY 2011) is the synthesis, characterization, and initial testing of selected catalyst materials.

Results of initial testing of Pd-based catalysts clearly show that selectivity toward the formation of CO and CH_4 can be varied systematically by changing the metal dispersion on the alumina support. High resolution transmission electron microscopy images revealed that atomically dispersed Pd was present on the alumina support at loadings lower than 1%, while nanometer-sized metal clusters were observed at 10% loading. Palladium atomically dispersed on the oxide support catalyzed the reduction of CO_2 to CO with above 90% selectivity, while CH_4 was produced on large metal clusters with higher than 90% selectivity. Catalytic testing of carbon nanotube-supported palladium catalysts revealed the critical role that oxides play in the CO_2 reduction process: no CO_2 activation was observed without the addition of an oxide promoter to the Pd/C nanotube system. These results have provided valuable information to guide FY 2012 research, which is aimed at understanding and utilizing the effects of oxide modifiers on the catalytic centers.

Also during FY 2011, PolyOligoSileSquioxane (POSS) molecules that will serve as core building block architecture were synthesized and preliminarily characterized by nuclear magnetic resonance. The molecules that were targeted for initial synthesis were developed by a combination of sol-gel synthesis and post-synthetic modification of the functionalities to introduce desirable R groups such as ($–CHNH_2$-CH_2NH_2), ($–CHPPh_2$-CH_2PPh_2), ($-CH_2NH_2$). The introduction of metals selected is based on their reactivities with CO_2 in homogeneous catalytic systems (Ru, Rh, Cu, and Ni). Detailed characterization of these systems by spectroscopic techniques is underway. Initial testing is currently performed with the catalysts synthesized thus far in polar aprotic solvents. The reactions are primarily being monitored by ^{1}H and ^{13}C NMR to determine turnover numbers and frequencies.

We will further our research in FY 2012 by creating fundamentally new properties by introducing the modifiers in to the active metal, support material, and around the coordination sphere around the active metal phase. We will continue to employ POSS molecules to prepare multi-functional catalysts with transition metals. Finally, we are systematically varying the hard and soft Lewis base adatoms to determine their effect on the efficiency and selectivity of the catalytic reduction of CO_2.

Non-Metal Activation of Hydrogen for Energy Storage in Chemical Bonds

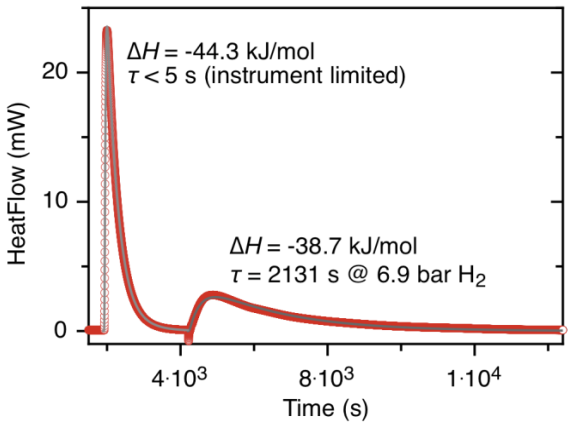
Donald M. Camaioni, Abhijeet J. Karkamkar, Kshitij K. Parab, S. Thomas Autrey, Bojana Ginovska-Pangovska

◆ Activation of small molecules such as hydrogen, carbon dioxide, methane, and nitrogen is critical for development of renewable fuels. This project aims to develop mechanistic understanding of the activation of hydrogen by non-metal Lewis pairs to be used in catalytic reduction of small molecules. ◆

While activation of hydrogen using transition metal catalysts is widely practiced, activation with non-metals is less common and little understood. This lack of understanding hinders development of new and inexpensive catalysts for energy storage applications. To solve this problem, we are working to characterize Lewis acid-Lewis base pair properties in solution and solid-phase environments relevant to hydrogen activation using a suite of experimental methods (nuclear magnetic resonance spectroscopy, calorimetry, and x-ray analyses) in combination with computational electronic structure methods (density functional theory and molecular orbital). This information will be used to develop simple predictive relationships. In addition, we are scouting for potential uses of this chemistry as a means to store energy in fuels and chemicals.

During project initiation in FY 2010, we analyzed the advantages of bifunctional systems in which Lewis acid and Lewis base are present in the same molecule to overcome energy and entropy penalties of forming a termolecular reactive complex. We screened several acid-base pairs, computing structures reaction paths and energetics. From this, we selected promising systems to target for synthesis and experimental study. We also commenced developing methodologies to measure parameters in the solution phase using select solvents capable of solvating both adduct and ion pair. Finally, we studied the effect of temperature on rate of ion-pair formation.

During FY 2011, we obtained results in three thrust areas: theoretical modeling of structure and reaction paths, reactivity and thermochemistry in solution, and kinetics of hydrogen activation. Our computational studies were aimed at understanding the pathways of prototypical reaction of hydrogen with ammonia and a Lewis acid. We extended our theoretical studies to the related lutidine·BCl_3 Lewis pair and investigating the mechanism of H_2 activation experimentally, observing H_2 activation for the first time. Lutidine·BCl_3 does not activate H_2 at room temperature but above 85°C, we observed the formation of lutidine·$BHCl_2$ and lutidinium BCl_4^-. Calculations show that the dative bond in lutidine·BCl_3 is ~12 kcal/mol consistent with the need to heat the reaction to break the dative and allow formation of the precursor to H_2 activation. However, we do not observe the putative ion pair, [lutidineH^+][$BHCl_3^-$]. Instead, it appears to redistribute ligands with lutidine·BCl_3 to give the observed products.



Heat flow trace from reaction calorimeter for dative bond formation and hydrogenation of 2,6-lutidine-tris(pentafluorophenyl)borane Lewis pair.

Simultaneously, we developed methods to measure thermochemistry and kinetics for the processes involved in the hydrogen activation by frustrated Lewis pairs (FLPs) using calorimetry and nuclear magnetic resonance spectroscopy. A new capability extracts the reaction rate constants from the time dependence of heat flow measured by an isothermal reaction calorimeter. Results are obtained by reacting 2,6-lutidine with tris(pentafluoro-phenyl)borane, $(B(C_6F_5)_3$ in bromobenzene solvent, followed by reacting this solution with 100 psi H_2 gas. Analysis of the heat flow shows that the rate of dative bond formation is limited by the instrument response, but the hydrogenation reaction exhibits a heat flow trace that is convoluted with the slow release of heat from reaction with H_2. Deconvolution of data with a psuedo-first reaction rate model provided a lifetime of ~2100 s for hydrogenation of the dative pair corresponding to a second order rate constant of 7×10^{-5} $s^{-1}atm^{-1}$. This rate is not limited by diffusion of H_2 into the solution since the researchers have measured shorter lifetimes for hydrogenation other FLPs.

In FY 2012, we will continue the above thrusts and begin a new on hydrogenation of unsaturated compounds using Lewis pairs with the purpose to evaluating the requirements for catalytic hydrogenation H_2 by Lewis acid-Lewis base pairs. We will investigate requirements for the transfer of hydrogen from ion pairs to unsaturated molecules, characterize solvent effects on Lewis pairs, and evaluate effects of solvation on H_2 activation. Additionally, we will work to publish our findings in peer-reviewed journals.

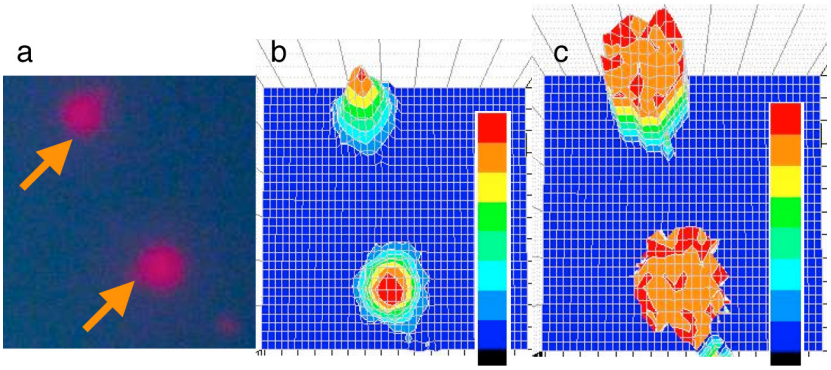
Oxygen Optode for Chemical Imaging in Microfluidic Microbial Models

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

◆ Microorganisms that play crucial roles in nutrient, geochemical, and energy cycles on the earth do not act alone; they perform as members of microbial communities which experience spatial and temporal changes in redox state and redox gradients. This project is developing analytical methods based on fluorescent imaging (optodes) to observe oxygen concentrations and gradients within spatially structured microfluidic models that contain microorganisms. ◆

A new method of studying chemical concentrations and gradients within microenvironments focuses on fluorescent optodes capable of chemical imaging at specific locations and across planar areas. The optodes consist of polymer materials that contain chemically sensitive fluorescent dyes. Combined with advances in optical imaging techniques and digital instrumentation, current optodes extend the previous work in fluorescent fiber optic point sensors, and are compatible with recent advances in developing microfluidic flow cells as models of spatially structured heterogeneous environments.

This project is focused on sensing oxygen within pores and across gradients in pore-network micromodels serving as microhabitats for microorganisms. In developing this new measurement capability at PNNL, we investigated a number of fluorescent-sensing materials and formats. These have included a commercial sol-gel material and commercial polymer nanospheres as well as polymer microspheres we have synthesized and polymer films we have formulated. Key parameters for chemical mapping include oxygen, carbon dioxide, and hydrogen ion concentrations. Each of these parameters can be sensed optically using fluorescence measurements, where the luminescence of an optode material is dependent on the parameter of interest.



Images showing two fluorescent optode microspheres of 2-3 micron diameter using a) CCD image, b) scanning microscope plotting amplitude related to intensity, and c) scanning image plotting phase related to fluorescent lifetime; hence, oxygen concentration.

Devices to detect analytes were originally developed in FY 2009 as single-point sensors. Fluorescent sensors for gases and electrolytes were developed as single particle or bead sensors and are designed to be reversible, thus responding to changes in the sensed parameter. In developing a measurement capability in FY 2010, we investigated a number of fluorescent sensing materials and material formats. In FY 2011, we focused on platinum porphyrin containing polymer materials for sensitive oxygen concentration detection, where the fluorescent intensity and range of use depend in part on the polymer material permeability. We developed a methodology for incorporating planar polymer optode films into the fabrication and assembly of experimental micromodels with etched silicon pore network structures and borosilicate glass cover plates. The polymer optode film on the underside of the glass cover in contact with fluids in the micromodel can sense oxygen concentration in individual pores as well as detect fluidically generated gradients across the pore network width.

Aside from fluorescent films, this capability required several items of apparatus. We fabricated planar microfluidic flow cells and pore networks in polydimethylsiloxane, acrylic plastics, polycarbonate thermoplastic, and silicon using a range of techniques, including micromachining under dry etch conditions, micromolding, and imprinting. Some structures were created with inputs for oxygen-containing and oxygen-free water to enable creation of oxygen gradients. To deliver these solutions to the flow cell, we obtained fluidic equipment. We designed and constructed a laser scanning imaging station for optical measurements, enabling examination of fluorescent films in three distinct imaging modes – intensity, ratiometric, and lifetime. Oxygen sensing is based on reduced lifetime and intensity of fluorescence in the presence of oxygen. We focused on lifetime-based sensing as the preferred readout, which improved resolution of system, easily probing individual pores, which are typically about 100 microns in diameter and can image individual optode microspheres in the 2 to 4 micron diameter range.

Work during FY 2012 for this project will focus on the integration of oxygen-sensing films and particles into microfluidic habitats that growing microorganisms, in collaboration with other microbial communities projects. These methods will enable imaging oxygen gradients that are created fluidically or by microbial activity within the micromodel environment.

Speciation and Distribution of f-Elements for Enhanced Separations and Safeguards

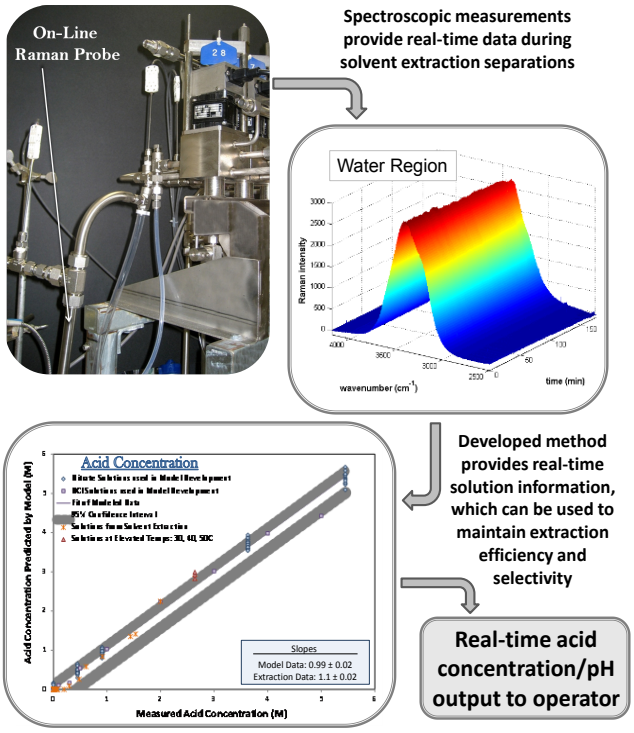
Amanda J. Casella, Tatiana G. Levitskaia, Samuel A. Bryan, James M. Peterson

◆ Extensive knowledge of real-time solution properties and composition are a necessity for any nuclear fuel reprocessing method. This work focuses on the coordination chemistry and interfacial transport behavior of lanthanides and actinides in various reprocessing schemes and the advancement of on-line spectroscopic techniques that can provide real-time monitoring of solution properties. ◆

Understanding the coordination chemistry and interfacial transport behavior of lanthanides and actinides in complex heterogeneous systems is required to design, characterize, and predictably model an f-metal separation system successfully. Currently, the chemical state of f-metals in liquid-liquid separation systems is focused on the acidic aqueous phase, but there is unfamiliarity with the chemical behavior of f-metal ions in corresponding organic media. With a chemical similarity between lanthanides and actinides, successful separation requires precise knowledge of the coordination and transport behavior in the complicated separation system and constitutes a challenging technical framework for the proposed investigation. Once acquired, this information can be translated to different separation processes.

Speciation and distribution behavior in PUREX-like nuclear fuel reprocessing schemes were investigated. Testing involved measuring the distribution behavior of extraction system constituents between aqueous and organic phases and speciation phenomena such as reduction/oxidation changes and interaction effects in the organic phase. The liquid-liquid distribution of several components in the equilibrium batch extraction experiments and in sub-equilibrium flow extraction using centrifugal contactors was compared. In the centrifugal contactor system, all inlet and outlet lines were instrumented with spectroscopic probes, allowing for continuous Raman and vis/NIR spectroscopic monitoring.

In nuclear fuel reprocessing separations, aqueous speciation of the target analytes and thus extraction efficiency and selectivity are strongly affected by pH/acid concentration. Therefore, monitoring this parameter is of critical importance for process quality and control. In nuclear fuel reprocessing facilities, classic potentiometric pH measurements are not suitable for real-time applications from requirements of frequent calibration and maintenance and poor long-term stability in the aggressive chemical and radiation environments. We thus developed a general method for determining pH/acid concentration of aqueous solutions by spectroscopic techniques, which utilized robust probes that can be installed directly into the stream and provide real-time monitoring capability. Application of this technique was demonstrated through a PUREX-like and a TALSPEAK-like separation scheme performed in a centrifugal contactor bank, equipped with on-line spectroscopy. Through analysis of the Raman data from the post-contact aqueous stream, the developed method determined the pH/acid concentration over a range of conditions for both separation schemes.



TALSPEAK (separation of americium and curium from rare earths) serves as a primary platform for understanding phenomena such as donor-acceptor interactions, chemical selectivity, and solute release during liquid-liquid extraction, leading to enhanced capabilities to monitor, predict, and model the solvent extraction process. TALSPEAK extraction chemistry of f-metals introduces kinetic constraints that may prevent the system from reaching local thermodynamic equilibrium in counter-current separation equipment such as centrifugal contactors, making it difficult to project batch contact data for flowsheet modeling. Research performed gained speciation and structural information on the organic phase under various loading conditions through combined spectroscopic and analytical analysis that benefits an overall improved prediction of process performance under sub-equilibrium flow conditions.

The Statistical Mechanics of Complex Process in Bulk and Interfacial Environments

Marcel D. Baer

◆ This project will develop new research capabilities for simulation of reactivity and structure in complex heterogeneous and homogeneous environments. ◆

A significant issue in basic energy sciences is understanding and characterizing the novel chemistry that takes place at interfaces. This requires the use of molecular simulation with interaction potentials that contain charge transfer, polarization, and the ability to make and break chemical bonds (i.e., chemistry). The development of novel simulation protocols to probe differences between bulk and interfacial environments is a crucial component to making quantitative predictions about reaction thermodynamics, selectivity, and activity. Understanding the nature of ion solvation at interfaces can change how we conduct basic energy research, however, fundamentals of an ion's propensity to be present at an interface and the important interactions are still not fully understood.

In recent years, theoretical and experimental studies have presented a picture of the aqueous interface, wherein hard and/or multiply charged ions are excluded from the interface, but large polarizable anions show interfacial enhancement relative to the bulk. Thus, a fundamental understanding of ions in solution is an important step toward controlling matter. Surface sensitive spectroscopy and current and next-generation x-ray absorption experiments require high quality simulations in order to interpret observation. Thus, there is a unique opportunity to use and develop molecular simulation methodology based in quantum mechanics to advance our understanding of these important systems and provide sorely needed data to aid in the interpretation of experiments. To this end, the air-water interface serves as a model interface where much of the important phenomena regarding ions and proton transfer are an active area of research.

We first address the proper simulation protocol to obtain stable air-water interfaces utilizing density functional theory. We have carried out first-principles molecular dynamics simulations of air-water interfaces employing a particular generalized gradient approximation to the exchange-correlation functional, with and without empirical dispersion corrections. We assess the utility of the dispersion corrections by comparing of a variety of structural (pair distribution functions, hydrogen bond populations), dynamic (diffusion constants), and thermodynamic (density) properties of bulk and interfacial water with experimental data as well as other first-principles and empirical force field-based simulations. These extensive calculations systematically benchmark the effect of dispersion corrected on the structure and dynamics of the extended air-water interface, showing a vast improvement for the dispersion corrected one. These results have been accepted for publication in the *Journal of Chemical Physics*.

Using the established protocol for the interfacial simulations, we constructed potentials of mean force of the transfer of iodide from the interior to the surface in both a cluster and the extended air-water interface. Our research supports a picture that empirical polarizable interaction potentials may overestimate surface adsorption for iodide. In conjunction with previous theoretical and experimental studies on iodide solvation, these results have implications toward the necessary interactions that give rise to the specific ion effect at the air-water interface and were recently published in the *Journal of Physical Chemistry Letters*. Further, a joint experimental and theoretical study reveal that molecular HNO_3 interacts remarkably weakly with solvating water molecules at low concentration; around 4 M, there is a turnover to a more structured solvation shell, accompanied by an increase in hydrogen bonding between HNO_3 and water. We suggest that the driving force behind the more structured solvent configuration of HNO_3 is the overlap of nitric acid solvent shells that sets in around 4 molar concentration. These results were published in the *Journal of Physical Chemistry B*.

Experiments show that dissociation of HNO_3 is decreased by approximately 20% near the solution interface compared with bulk, and further that dissociation occurs even in the top-most solution layer. These findings are supported by first-principles simulations, which show that hydrogen bonds between HNO_3 and water molecules at the solution surface stabilize the molecular form at low concentration, compared with the stabilization of molecular HNO_3 that occurs in bulk solution at high concentration.

We will continue to pursue a better understanding of complex chemistry at interfaces using molecular simulation. This includes but is not limited to continued development of interaction potentials and sampling methods toward characterizing experimental observables in concentrated acid and electrolyte solutions in bulk and interfacial environments. We will develop methods to calculate molecular properties like molecular polarizability and ion-radii from first-principle molecular dynamics simulations using DFT based interaction potentials that can be used in a continuum theory description.

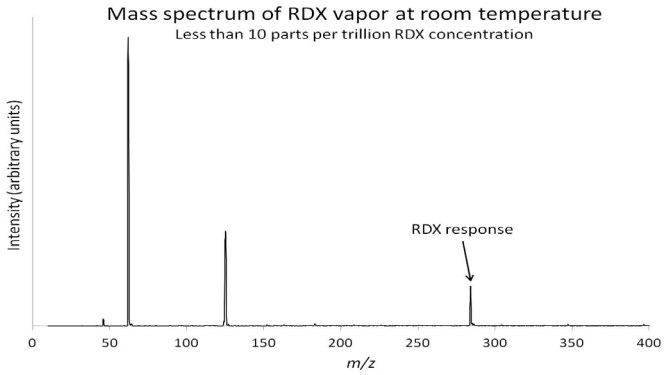
Vapor Detection of Non-Volatile Explosive Compounds by Enhanced Trace Analytical Methods

Robert G. Ewing, Melanie J. Waltman, Brian H. Clowers, M. Lizabeth Alexander, David A. Atkinson

◆ Direct vapor detection of low volatility explosive compounds will provide revolutionary advances in explosives detection capabilities while also enabling a non-contact sampling paradigm which removes human error and reduces manpower cost from screening activities. This project achieved substantial enhancement of targeted components and demonstrated direct vapor detection of PETN and RDX. ◆

Trace detection such as ion mobility spectrometry (IMS) widely deployed as an explosives detection solution for aviation security. IMS is currently the choice system based upon sensitivity, durability, and ease of operation. A challenge for trace detection is that it currently relies on physically swiping a surface to pick up non-volatile residue of explosive compounds. This method is dependent on operator skill and is man-power intensive. Non-contact sampling is a preferred method for screening people, luggage, and cargo. For non-contact sampling to be viable, trace detection would need to be able to directly detect explosive vapors (essentially the way that canines are used to detect explosives). Low-volatile explosives have saturated equilibrium vapor concentrations that are at or below the parts-per-trillion range. In a screening environment, it is unlikely that equilibrium concentrations would be reached, due to dilution from ventilation and reduction of vapor emissions due to packaging. Gains in sensitivity of 10^2 to10^6 would enable direct vapor detection by IMS or mass spectrometry. Incremental gains on each of several instrument components enable a system performance that could approach these levels. Methods to increase the sensitivity and selectivity were pursued for both IMS and mass spectrometry.

This work focused on enhancing the chemical ionization mechanisms, increasing the selectivity of the ionization process, and improving the ion transduction mechanism with subsequent increases in the signal-to-noise ratio, and thus enhanced detector performance. Along with IMS, mass spectrometry has the potential to perform direct vapor detection of explosives. Chemical ionization mass spectrometry has been widely demonstrated as a highly sensitive and selective laboratory technique for the detection of target compounds. Proton transfer reaction mass spectrometry is typically used for atmospheric contaminant studies since it measures concentrations of specific compounds below low parts per trillion. While proton transfer reactions in the gas phase enable these high levels of sensitivity, they are not reproduced when analysis is directed toward more electronegative gas phase species such as those found in explosives. A new, high-sensitivity bi-polar chemical ionization mass spectrometer based on the proton transfer reaction mass spectrometry design has been developed at PNNL. This instrument potentially allows product ion current to be increased by a factor of between 100 and 1000. This improvement leads to unprecedented real-time detection limits of less than 1 ppt_v. With a modified ionization source added to this instrument and other modifications to the electronics, negative ion currents of at least 200 picoamps were achieved.



Vapor detection of RDX at room temperature with no sample preconcentration.

Improvements in detection based upon increasing the signal-to-noise ratio in a Faraday plate was also explored, developed, and evaluated. A laboratory-built IMS system was used to evaluate the parameters of signal magnitude, absolute detector noise and response time. Additional parameters used for comparison of the different detector technologies include sensitivity, accuracy, precision, and linear dynamic range. The characteristics observed for the Faraday plate indicated a radial mobility discrimination of the ion cloud as it traversed the drift region. This observation was recorded using a segmented Faraday detector plate comprising of concentric rings. A second approach to improved signal detection provided an increase in the signal-to-noise ratio by a factor of about 2 over conventional Faraday plate detectors.

Demonstrated component level improvements have led to large advances in the detection of explosives vapors. These advances were demonstrated through the direct vapor detection of a fingerprint quantity of RDX and PETN. This is a revolutionary breakthrough in explosives detection and further refinement should result in a paradigm shift in how screening operations are performed.

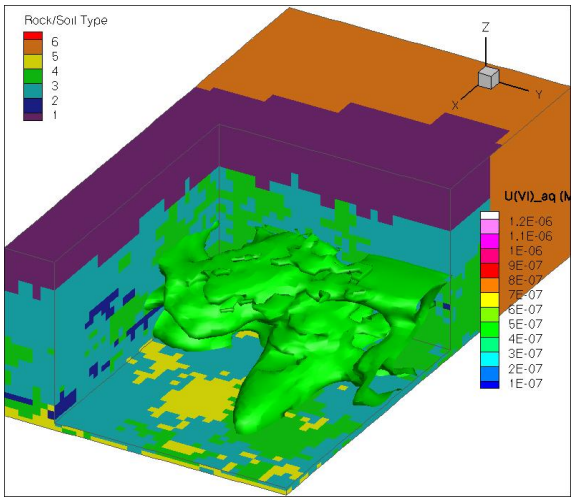
Earth and Space Sciences

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

Steven B. Yabusaki, Yilin Fang, Bruce J. Palmer, Guang Lin, Anderson L. Ward, Timothy D. Scheibe

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

Reactive transport simulation codes have become widely used for simulating the movement and fate of contaminants and other dissolved constituents in the subsurface. They are useful not only as engineering tools for site analysis but also, importantly, as fundamental research tools. While major advances have been made in our ability to simulate numerically complex hydrologic, geochemical, and microbiological processes of interest, accurate and detailed characterization of spatial property distributions in the subsurface remains the primary challenge facing reactive transport modeling efforts. The extreme resolution targeted for computation-based research on critical subsurface science issues requires highly scalable simulators that can fully exploit the high performance and large memory of the most advanced computers.



Simulated removal of aqueous U(VI) by indigenous metal-reducing bacteria after 40 days of biostimulation. The isosurface shows the effect of spatially variable material properties in cutaway surfaces on the engineered bio-immobilization of uranium in a shallow alluvial aquifer.

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

In FY 2009, a parallel processing operational mode for variably saturated flow and multicomponent reactive transport, eSTOMP-H_2O, was successfully developed. Scalability was demonstrated across 16,384 processor cores on both the EMSL Chinook and NERSC Franklin clusters. The general restructuring approach from the previous year was used in FY 2010 to develop and successfully test the non-isothermal, multiphase, multifluid eSTOMP-CO_2 operational mode for deep geologic CO_2 sequestration. Application and development of eSTOMP-H_2O also continued. The successful simulation of a uranium bioremediation field experiment was one of the most complex, coupled-process, field-scale, reactive transport simulations of its kind. A multilevel parallelism simulation framework based on GA processor groups was applied to uncertainty quantification in the Hanford 300 Area aquifer: 317 alternative conceptual model simulations in 23 hrs using 4096 processors vs. 1 week for a single desktop simulation. A new load balancing scheme based on GA counters was implemented to address spatially variable computational "hot spots" of reaction solver activity. A new project with Professor Warren MacEvoy investigating the use of GPUs for reaction-dominant simulations successfully developed and tested a differential algebraic equation solver on Nvidia Tesla systems at Mesa State College and PNNL. The conclusion is that this is a viable approach for current and future general purpose GPU architectures.

In FY 2011, successful proposals for time on the DOE EMSL Chinook and OLCF Jaguar led to eSTOMP scaling studies using up to 131,040 processors. eSTOMP was one of four codes selected for the FY 2011ASCR Software Metric for Computational Effectiveness to OMB. eSTOMP-CO_2 applications included $scCO_2$ injection and entrapment in heterogeneous sandstone formations. Multi-level parallelism using GA processor groups was used for an uncertainty quantification study where the simulation time for 128 realizations of heterogeneous material properties was reduced from weeks to less than one day. Additional eSTOMP capabilities under development include a multilevel parallel eSTOMP hydrologic inverse modeling methodology (based on the PEST parameter estimation infrastructure) and nonisothermal, two-phase flow.

Computational Framework for Diagnostics, Validation and Intercomparison of Numerical Simulators for Geologic Sequestration

Mark D. White, Kenneth C. Carroll, Chandrinka Sivaramakrishnan, Sumit Purohit

◆ This research will develop a computational framework that provides access to benchmarking, validation and code intercomparison problems/case studies for geologic sequestration of greenhouse gases. Problems and case studies selected for the framework will be internationally recognized, along with new contributions created through the project. ◆

Numerical simulation capabilities for modeling sequestration processes associated with the fate of greenhouse gases injected into geologic reservoirs has evolved rapidly. At the start of the last decade, the accepted state of the science was numerical simulators that could address dissolution, structural, and mineralization trapping, isothermal conditions, aqueous-based geochemistry, and decoupled geomechanics for idealized conceptualizations of the subsurface. The standard for geologic sequestration modeling is continually advancing but now includes capabilities for predicting hydraulic trapping, nonisothermal conditions, transitions to subcritical conditions, ground-surface interactions, injection wells, co-sequestration, supercritical CO_2-based geochemistry, coupled hydrology-geochemistry-geomechanics, heterogeneous basin-scale domains, and wettability transitions. A critical component associated with developing analytic tools is the verification, benchmarking, and validation of computer code and implementing mathematical models and numerical solution schemes.

This project is developing a computational framework that makes validation and benchmarking a dynamic process where numerical solutions evolve with modeling capability advances and benchmark problem complexity evolves with growth in available field and experimental data. We will produce a computational framework for diagnosis and intercomparison, a suite of validation problems and solutions, observational data sets for model validation, standardized documentation of code features and characteristics, and systematic accounting of disagreements for validation problems.

The national laboratories have developed and are continually improving a suite of numerical simulators for modeling geologic sequestration of greenhouse gases that collectively represent the state of science and coupled-process modeling. Our project began with three principal foci: assimilate validation problems, acquire and install four national laboratory codes on the GS^3 server, and identify new scientific research directions for extending the current suite of code comparison problems for geologic sequestration. Each new research direction required support from the experimental component In Situ Sequestration Suite (IS^3). We made substantial advances on the experimental data collection and mathematical model development for understanding multifluid geochemistry.

In FY 2011, we developed a dynamic framework and assimilated internationally recognized problems and numerical simulators for geologic sequestration into the framework. We also completed a prototype framework that provided access to problems/case studies through a geographic or process map. The geographic interface allows users to locate problems/case studies via geologic location or source, and the process map locates problems and case studies in a grid of coupled-process squares with increasing complexity on the abscissa and increasing scale on the ordinate. For the process map, a grid of 12 coupled process squares were defined from four principal geologic sequestration processes: multifluid hydrologic, geomechanics, geochemistry, and heat transfer. Problems/case studies were identified on either map as the familiar tack pins that when selected provide the user with general problem/case study information, descriptions, and references as well as specific problem/case study inputs, outputs, data sets, and visualized outputs for a selected group of internationally recognized numerical simulators for geologic sequestration.

We directed a majority of the labor effort during FY 2011 at assimilating a collection of internationally recognized problems/case studies and applied a collection of internationally recognized numerical simulators to those problems/case studies. We completed four problems using six numerical simulators: FEHM from LANL, OpenGeoSys from HCER, PFLOTRAN from LANL, STOMP from PNNL, TOUGH from LBNL, and VESA from University of North Carolina. The key observation from FY 2011 is that expertise of applying various simulators to recognized problems/case studies needs to be captured for future reference.

For FY 2012, our emphasis will shift to becoming more proficient with a suite of internationally recognized numerical simulators for geologic sequestration. The overarching objective is to develop a computational framework that provides users with access to a suite of problems/case studies for benchmarking and validating numerical simulators for geologic sequestration. Our initial target of numerical simulators are those developed at DOE national laboratories as well as internationally non-commercial codes. We will develop a computational framework for benchmarking and validation of the STOMP-CO_2 and STOMP-CO_2e simulators fully integrated into GS^3 using internationally recognized problems/case studies and use their unique capabilities in the to define new problems/case studies.

Data Assimilation Tools for CO_2 Reservoir Model Development

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

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

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

The objective of this research is to build workflow and software tools that support data analysis and assimilation tasks for the development and parameterization of models of subsurface reservoirs for CO_2 sequestration.

In the first year of this project (FY 2010), we interfaced with a software framework group to design the layout and recommend features/capabilities to incorporate into the GS^3 wiki. We composed a technical report that reviewed key data types, analyses, and selected software for reservoir model development. In addition, we developed or linked to existing rock and fluid property databases and created programs and scripts for tasks associated with data analysis and assimilation.

During FY 2011, we developed and implemented additional software tools within the GS^3 wiki. Accomplishments are described below.

- Two CO_2 plume area calculation programs were developed and implemented with the GS^3 wiki. The first plume calculator, which accounts for mixing but does not account for buoyancy effects, allows a user to enter information about injection depth, temperature, salinity, porosity, and injected mass of CO_2. It then calculates plume area with the results being viewable from the GS^3 wiki via Google Maps. The second plume calculator uses an analytic solution for a sharp-interface model that accounts for buoyancy effects, but neglects mixing. This calculator is thought to yield conservative plume estimates (maximum spreading). Its results are also viewable from the GS^3 wiki via Google Maps.
- In addition, log ASCII standard (LAS) file plotting and viewing were made operable from GS^3 wiki. LAS files are a standardized format for geophysical well log data, and programs were developed for reading and plotting LAS files. In conjunction with staff from the GS^3 platform project, we developed capabilities for invoking LAS file plotting from the GS^3 wiki and viewing well locations on Google Maps.
- An R-based multivariate analysis toolkit was developed that consists of algorithms for performing different types of statistical analyses: descriptive statistics, correlation, classification, and prediction. The capabilities include principal components analysis, cluster analysis, and neural network modeling. This multivariate toolkit is applicable to analyzing several different types of geologic and geophysical data used in the development and parameterization of numerical models of CO_2 sequestration and can be invoked from the GS^3 wiki.
- A graphical user interface (GUI) for model attributes has been developed in Jython. It includes worksheets for the following categories: general site description; infrastructure and operations; geologic framework; processes and properties; and monitoring, history matching, and model comparisons. The model attributes defined through this GUI pertain primarily to the site conceptual model and the data used in its development, which are also used for parameterization of numerical models. This GUI can also be invoked from the GS^3 wiki.
- We also developed a version of the model attributes GUI for the Sim-SEQ project, a multi-agency and multi-national project on CO_2 sequestration and model development that is being led by Lawrence Berkeley National Laboratory.
- A prototype geophysics toolkit was implemented in Matlab to perform various tasks related to site characterization and monitoring, including viewing seismic data (e.g., SEGY files), developing synthetic seismograms, modeling and interpretation of vertical seismic profiles, and identification of reservoir and cap rock intervals.

- And finally, a prototype rock properties catalog was developed for physical, hydraulic, and mineralogical property data of selected reservoir formations and cap rocks. This prototype rock properties catalog is currently in Excel spreadsheets, but the development of a data model for a wiki-based repository has been under discussion. The spreadsheet data are augmented by URLs to publically accessible external databases. This rock properties catalog will likely be superseded by a similar one that has recently been developed by others on a project funded by DOE's National Energy Technology Laboratory.

Developing Ice Nucleation Parameterizations for Large-Scale Models

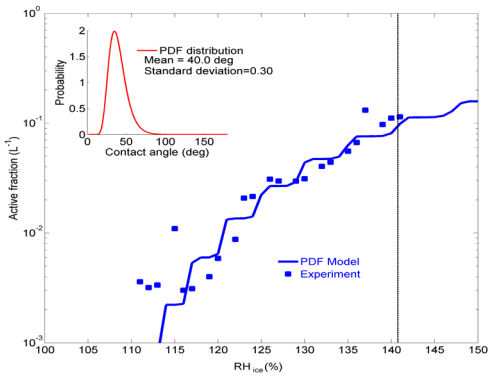
Xiaohong Liu, Gourihar R. Kulkarni, Jiwen Fan,
Jennifer M. Comstock, Mikhail Ovchinnikov

◆ We propose to develop a new ice nucleation parameterization so that we can quantify the climatic impact of aerosol effects. Such a parameterization will improve representation of aerosol-cloud interactions in cloud-resolved, regional, and global models. ◆

More than half of the global precipitation originates from the ice phase. Because primary ice particles are formed on a tiny fraction (10^{-5}) of atmospheric particles (called ice nuclei), natural and human activities can potentially impact ice formation in the atmosphere, leading to the alteration of earth's energy budgets and hydrological cycles. The limited information about ice formation processes limits our ability to forecast precipitation production and to predict climate change. While aerosol influence on cloud droplet nucleation has received considerable attention from the climate research community, the effects of aerosol particles on ice formation present another challenge for observations and modeling. It is clear, however, that nucleation is important to initiating precipitation and influencing cloud microphysical and radiative properties.

Our objective was to develop a new ice nucleation parameterization from first principles with constrained classical nucleation theory (CNT). The parameterization was applied in mixed-phase and ice cloud regimes for aerosols (mineral dust) acting as ice nuclei through deposition nucleation mechanism. We investigated the dependence of ice nucleation on dust sizes at different temperatures. This new parameterization was used in a cloud-resolving model to explore the aerosol effects on ice clouds. We developed a close collaboration between observers and modelers at PNNL from the fundamental understanding of ice nucleation in the laboratory to the improved parameterization in climate models.

In the first year of this project, we collected experimental data on ice nucleation published in the literature. The data contained the ice nucleation onset conditions (temperature, relative humidity, and aerosol particle size) of mineral dust particles investigated under deposition nucleation freezing mechanism. We also collected ice nucleation data from the newly developed ice chamber at the PNNL Atmospheric Measurements Laboratory, where different sizes of mineral dust (Arizona test dust and Kaolinite) at 100, 300, and 500 nm diameter were selected and forwarded to the ice chamber. Active fraction (F_{ice}) was calculated as the ratio of ice number measured to total dust particles entering the chamber.



Active fraction of ATD particles as a function RHice. The experiment was carried out at -35°C and a 400 nm size. The solid curve shows the PDF model fit to the experimental data points; the inset shows the distribution with corresponding parameters. Vertical dashed line indicates the water saturation onset. The error in the RHice conditions is approximately ±3 %.

In FY 2011, we computed the contact angle between the ice embryo and ice nucleus-based on the CNT using experimental data for deposition nucleation of mineral dust particles. The benefit of using CNT is that it includes a specific link between the nucleation rate and aerosol properties (i.e., size and composition). We also modified the CNT to introduce the probability distribution function (PDF) of contact angle to reflect the complexity of particle surface inhomogeneity. The PDF parameters mean (μ) and standard deviation (σ) were derived by fitting the computed F_{ice} to measured F_{ice} values. We implemented the CNT with the PDF of contact angle in a cloud-resolving model. Model simulations for a cirrus case at the DOE Atmospheric Radiation Measurement Southern Great Plain site were conducted. The sensitivity of modeled cloud microphysics properties (i.e., ice number concentration, ice water content, and cloud initiation times) to PDF distribution parameters and initial dust ice nuclei concentrations were analyzed. A scientific paper documenting the above results has been submitted to the journal *Atmospheric Chemistry and Physics*.

Combined with field observations through CNT, we made use of the most recent data from laboratory measurements to constrain the uncertain parameters. The parameterization is applicable to different temperature regimes (ice and mixed-phase clouds) and accounts for different mechanisms (immersion and deposition), depending on aerosol surface properties due to aging in the atmosphere. We expect that this new parameterization will be used in the next generation of regional and global models, which will add the capability to study aerosol effects on mixed-phase and ice clouds.

Development of Climate Modeling and Integrated Modeling at Regional Scales Framework and Functional Specifications

Ian Gorton

◆ We are designing a flexible software framework to integrate existing global models with high resolution regional models of climate, land usage, building energy demand, and power demand and supply. ◆

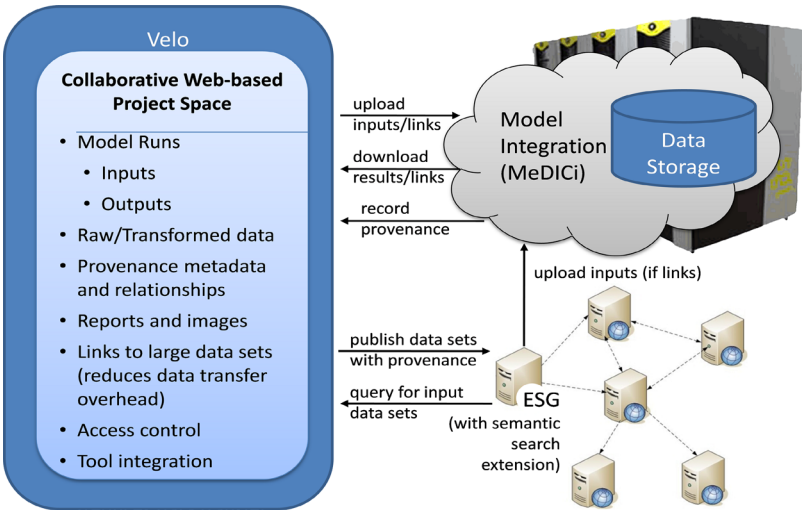
Global models of climate and integrated assessment address large-scale questions to understand the physical, biophysical and socio-economic consequences of climate and its interactions with human systems (e.g., climate and land use or land cover). Global models are ill-suited, however, to address regional-scale questions on impacts, adaptation, and mitigation. This project will result in a flexible software architecture that will allow model components with disparate temporal and spatial resolutions to pass information in a dynamic fashion. The functional specifications for both the operational (software engineering) and systems (socio-economic, climate, energy, ecosystem) components will be defined and implemented.

This project's software integration framework will link the various models involved in the Integrated Regional Earth Systems Modeling (iRESM) program, which consists of the following models: regional climate, regional assessment, building and land use, and energy infrastructure. All of these models work on different spatial and temporal scales, and are not designed to be linked in terms of input data required and output data produced. They also have radically different run time platforms from supercomputers to workstations and are built using multiple software programming languages. Together, these differences make model linking highly complex. In addition, model outputs for runs of several decades can be in the hundreds of megabyte to terabyte range, making the filtering, transformation, and transfer of data between models difficult.

In developing the modeling framework and functional specifications for the iRESM model, design is crucial. The framework will be planned so that the capability can address four overarching issues: 1) regional constraints on mitigation and adaptation, 2) effect of changes in regional average or extreme climate states on mitigation and adaptation, 3) interactions between management and natural processes that contribute to rapid or nonlinear environmental change, and 4) potential interactions between mitigation and adaptation decisions. We are investigating detailed scientific use cases, software integration, and data issues relevant to the integrated modeling environment. The overall goal is to implement the model framework to enable regional modeling scenarios for set up and execution.

During FY 2010, we worked extensively with iRESM modeling projects to understand current and planned capabilities and to analyze the scope and complexity of the required integration framework. To drive this analysis, we defined an initial use case to address. Based on this topology of model integration, we worked to define the various data requirements to understand the complexity of data transformation algorithms, the frequency with which the various models must exchange data as a simulation progresses, and mismatches in the data. These investigations drove the design of a prototype integration framework that demonstrates the feasibility of model integration in a simple, one-way fashion.

In FY 2011, we worked extensively with the iRESM modeling projects to document their data requirements and the needs for data transformations between models. This information fueled the design of a knowledge management platform for iRESM, based on our Velo technology and an integration platform based on our MeDICi Integration Framework (MIF). Specifically, we deployed a Velo instance for iRESM and have begun to populate the web site with data pertinent to the various models in iRESM. Each model has its own set of Web pages that document its use, link to the data sets it requires for a given regional modeling scenario, and has a web form that



The iRESM platform.

allows the user to execute any associated data transformations needed to run the model, as well as invoke the model itself. When the user invokes a data transformation or model execution, the Velo web page executes a script for a defined MIF pipeline for executing the series of computational jobs required for the task, and capturing the results as links to the Velo web page. This provides iRESM modelers with a simple and convenient method for managing and sharing model executions and results.

Velo also offers iRESM modelers the capability to start discussions on the various pages associated with a modeling experiment. Permissions can be set to control which users can see the pages associated with an experiment, and hence contribute to a discussion. In this way, Velo significantly enhances the collaboration between the team of modelers working on iRESM experiments. As this work progresses, the iRESM Velo site along with its integrated model execution capability (through MIF) will become the key knowledge management resource for teams of modelers working on complex regional model experiments.

Development of Coupled Flow, Thermal and Geomechanical Capability for Carbon Sequestration

Yilin Fang, Zhijie Xu, Steven B. Yabusaki

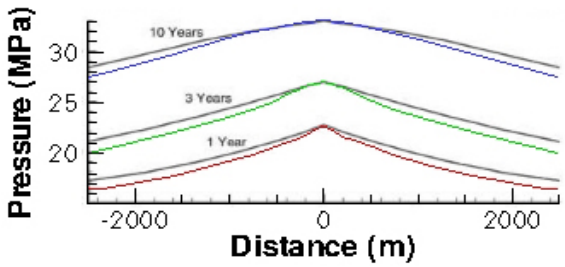
◆ This research is focused on developing critically needed geomechanical capabilities to address key research issues in carbon dioxide (CO_2) geological sequestration. This project will develop PNNL capabilities in large-scale subsurface simulation. ◆

Geologic sequestration of CO_2 is an attractive option for reducing greenhouse gas emissions without adversely influencing energy use. However, high pressure during the injection phase can result in large displacements of pore fluids and large stress changes on natural fractures and faults. A major risk associated with CO_2 sequestration is the potential leakage of CO_2 through the cap rock and overburden, which can lead to the release of CO_2 into shallow potable aquifers or to the atmosphere. Developed at PNNL, subsurface nonisothermal, multiphase flow, and reactive transport code (STOMP) does not have the capability of geomechanical simulation, which is critical to evaluate the overall suitability of the geological reservoir for safe CO_2 injection and the long-term subsurface containment of CO_2.

In this project, we are developing a simulation tool that couples nonisothermal fluid flow and geomechanical deformation processes to address key research issues in CO_2 geological sequestration. A particular interest is to develop a large-scale subsurface simulation that will eventually be used to evaluate the long-term sealing ability of caprock and fracture networks above target CO_2 storage reservoirs during CO_2 injection and storage. Geomechanical risks such as opening of pre-existing fractures, rock fracturing, weakening of the strength of faults, and induced seismicity increase along with pressure increases in the reservoir during CO_2 injection.

One methodology for our approach to reducing greenhouse gas emitted by coal-fired power plants is to capture the gaseous CO_2 effluent and inject it into deep geologic reservoirs as $scCO_2$. Initial analyses rely on predicting the evolution of effective stresses in rocks and faults during CO_2 injection. Potentially hundreds of supercritical CO_2 injection wells will operate in the Illinois Basin, and analysis will be necessary to determine the collective impact of these long-term injections and the aggregation of scCO2 beneath the caprock on structural integrity.

Our first steps incorporated a geomechanical model into the existing parallel subsurface nonisothermal, multiphase flow and reactive transport code (eSTOMP-CO_2) to provide coupled geomechanical and multiphase flow capabilities for the suite of simulation tools. Enhanced discrete element methods (DEM) at the mesoscale are used to examine the structure-property relationship in and close to individual fractures, capture the relevant dominating micro-mechanisms that cannot be accurately treated at larger scales, and provide reliable and robust submodels for model integration. Additional methods will be developed to couple models at the mesoscale and continuum scale.



Fluid pressure along the bottom of the injection aquifer (top lines are from the literature; others are from the results of our simulation).

Also during FY 2011, we incorporated a geomechanics code, Rigid-body Interface Element Method (RIEM), into the existing parallel subsurface nonisothermal, multiphase flow and reactive transport code (eSTOMP-CO_2) for linear and nonlinear problems. RIEM uses an unstructured grid, finite volume approach; however, it is a consistent superset of the eSTOMP formulation (i.e., the same grid can be used for RIEM and eSTOMP applications). We tested the linear problem using a benchmark problem in the literature that uses multiphase flow and transport code developed at LBNL, coupled with the commercial software for geotechnical analysis of soil and rocks. We also developed a simplified analytical model to solve geomechanical modeling of CO_2 geological sequestration that considers the poroelastic effects, accounting for the two-way coupling between the geomechanical response and fluid flow in greater detail. To date, our research has produced a paper on the analytical model has been submitted to the journal *Physical Review E*.

In FY 2012, we will continue testing the coupled geomechanical model with the parallel STOMP code and will apply the code to selected geological sequestration test sites. We will extend our simplified hydro-mechanical model to stress analysis in the caprock. Additionally, we will enhance our discrete element methods at the meso-scale to examine the fundamental physics relevant to rock deformation and fracturing, fluid flow, and process coupling, and capture the relevant dominating micro-mechanisms.

Development of Lidar-Based, Fine-Scale Three-Dimensional Wind Measurements to Advance Fundamental Understanding of Near-Surface Winds for Climate and Other Models

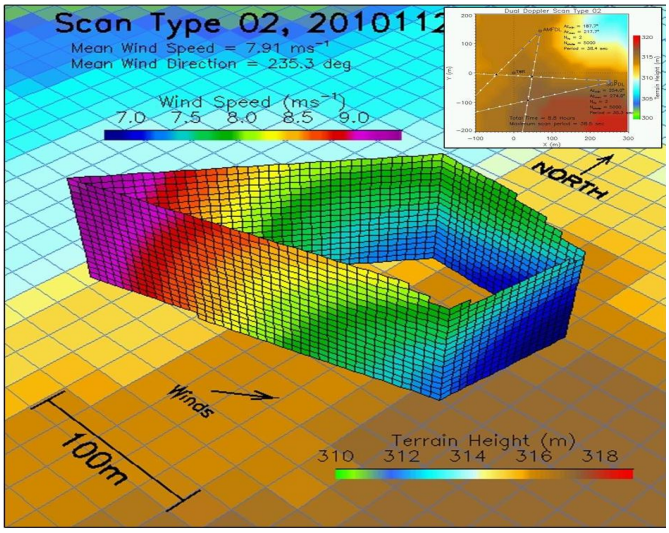
Rob K. Newsom

◆ With the rapid development of wind power underway, there is urgency to identify meteorological observational systems capable of mapping local wind resources accurately and efficiently. To address this need, this study explores the use of new lidar remote sensing techniques for fine-scale wind measurements within height layers of relevance to the wind energy industry (i.e., the lowest 200 m of the atmosphere). ◆

Traditional methods of wind resource assessment have typically relied on the use of instrumented towers, which provide measurements only along a single vertical profile in the atmosphere. By contrast, new lidar remote sensing techniques can be used to measure the full three-dimensional structure of atmospheric flows, thus providing a more complete picture of the local wind resource. Measurements such as these can be used to improve micro-siting and used for the development and evaluation of wind turbine designs.

The goal of this project is to develop and evaluate methodologies for three-dimensional measurements of micro-scale wind fields using scanning dual-Doppler lidar. Data for this study were acquired at the DOE Atmospheric Radiation Measurement (ARM) Southern Great Plains (SGP) site in north-central Oklahoma in late 2010. The key observational platforms include one heavily instrumented 60-m tower and two scanning coherent Doppler lidars, which provided range-resolved measurements of radial (line-of-sight) velocity. These lidars were used to scan the space around the 60-m tower, which was regarded as a proxy wind turbine. Radial velocity measurements from the two lidars are processed by a wind field retrieval algorithm to produce estimates of the three-dimensional wind field. To assess their accuracy, the retrieved winds were compared with independent wind measurements at various levels on the 60-m tower.

Over 60 hours of dual-Doppler lidar data were collected during both daytime and nighttime and under a variety of meteorological conditions. Scan strategies were setup such that each lidar performed sequences of repeated range-height indicator (RHI) scans at two closely spaced azimuth angles. The intersections of the scan planes defined a so-called "virtual box." Two approaches for estimating three-dimensional velocity fields from the raw dual-Doppler data were developed and tested. The first approach involved modeling the velocity field as an expansion of orthogonal basis functions, in which the expansion coefficients were



Three-dimensional view of wind speeds retrieved from dual-Doppler lidar data. The inset shows a plan view of the field site with the locations of the tower and two lidars. Lines indicate the direction of RHI scans, the planes and intersections of which define a "virtual box." Wind speeds are retrieved along the box surfaces and extend to a maximum height of 100 m above ground level while terrain heights decrease gradually from east to west across the box. In this case, there is a significant gradient in wind speed, which appears to correlate with the subtle variation in terrain height.

treated as adjustable parameters. The expansion coefficients were determined by minimizing the mean squared difference between the measurements and the line-of-sight projection of the modeled velocity field. With this approach, it was possible to impose mass conservation as a hard constraint, thus allowing for direct retrieval of the vertical velocity component, in addition to the horizontal components. However, results were found to be sensitive to the choice of the domain size and number of expansion terms.

An alternative approach was developed that was conceptually simpler but did not allow for direct retrieval of the vertical velocity component. This approach required estimating the radial velocity field from both lidars at prescribed grid points on the surfaces of the virtual box. By neglecting the vertical velocity component, the horizontal velocity vector (at each grid point) was easily computed from the two radial velocity estimates. Radial velocities between scan intersections were estimated using a distance-weighting scheme. This retrieval technique proved to be more robust and reliable than the first approach described above.

Analysis and three-dimensional visualization of the retrieved wind fields indicate correlations between horizontal

variations in wind speed and subtle terrain height variations. These results suggest that even small variations in terrain height can lead to significant horizontal heterogeneities in the wind speed. To assess their accuracy, the retrieved winds were also compared to independent wind measurements on the 60-m tower. The measurements were obtained from sonic anemometers mounted at the 25- and 60-m levels. Results indicate very good (>0.95) correlation between the sonic anemometer data and the lidar-derived winds. However, the lidar-derived winds tended to exhibit a slow bias with increasing wind speeds. For winds <10 m/s, the slow bias was small (<0.5 m/s), but as wind speed increased >15 m/s, the bias exceeded 1 m/s in many cases. It is believed that this effect was not caused by the retrieval algorithm but rather by an inherent bias that arises when the true radial velocity approaches the instrument's Nyquist velocity.

Development of Prototype Integrated Earth System and Environmental System Models

Lai-Yung (Ruby) Leung

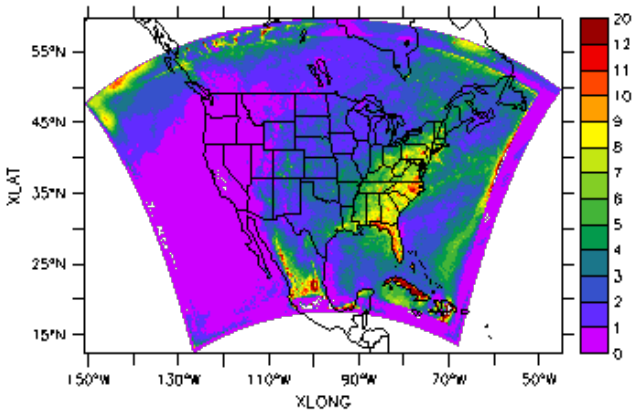
◆ This research will provide a new modeling capability to represent interactions between the atmosphere, ocean, terrestrial ecosystems, sea ice, and biogeochemical processes that allow us to investigate climate change impacts at the regional scale. ◆

Global climate models (GCMs) are the primary tools used to predict the evolution of the climate system. Through decades of development, GCMs have demonstrated the useful skill of simulating the global mean temperature response to various natural and anthropogenic forcings of the last century. More recently, global earth system models (ESMs) that integrate multiple climactic processes have emerged to enable the global carbon cycle to be included for projections of global climate change at the century time scale. Further, some progress has been made in demonstrating potential skill in climate predictions at the decadal time scales. Despite these efforts, our ability to understand and predict regional climate change and its impacts on the adaptive capacities and vulnerabilities of environmental and human systems is still limited because current GCMs/ESMs do not represent the myriads of human-earth system interactions that influence global and regional climate change. In addition, important human-earth system interactions that manifest at the local to regional scales cannot be explicitly represented in global models that have limited grid resolutions because of the hydrostatic formulation and computational constraints.

This project aims to develop the prototype models to represent regional earth system processes and the environmental systems. This project includes the development of two major components: the Regional Earth System Model (RESM) and the environmental system models of the integrated Regional Earth System Model (iRESM). The RESM will provide downscaled climate simulations to assess climate impacts and adaptation options. For this component, we will couple state-of-the-science community models of the regional atmosphere and aerosol/chemistry, ocean, land, and sea ice through a flux coupler to represent regional earth system processes and their interactions. The RESM will also include representations of land use and water use that fully interact with the natural water and biogeochemical cycles to characterize regional human-earth system interactions that are critical for projecting regional climate change.

For the second component, we will develop a fully integrated environmental system model for RIM to assess local/regional mitigation and adaptation strategies. Motivated by the need to reconcile the ubiquitous redundancy and inconsistency that exists across hydrology and ecosystem models in their representations of water and biogeochemical cycles, we will develop a model to represent hydrology, soil, managed and unmanaged ecosystems, and biogeochemical processes in a single modeling framework. The model will be scalable to the extent supported by data to enable coupling with the integrated human system models to capture human and earth system interactions at a wide range of scales. Additionally, this model will be based on the Community Land Model (CLM) that is also used in the global and regional earth system models. For scalability, we will develop a distributed extension of CLM (DCLM), incorporate more detailed water management in DCLM that takes advantage of the distributed framework, and couple DCLM and a crop model for more detailed representations of the managed ecosystems and land management.

During FY 2011, we continued our work from FY 2010, and progress was made in several areas. On development of a prototype RESM, the Weather Research and Forecasting (WRF) model has been coupled with CLM through a flux coupler. The model has been configured for a western U.S. domain at 12 km resolution. A simulation for one year has been performed and compared with observations and another WRF simulation that used the Noah land surface model instead of CLM to represent land surface processes. The WRF-CLM simulation compares quite well with observations and is similar to the WRF-Noah simulation except for a somewhat larger warm bias. Following this test, another domain for the conterminous United States at 20 km was configured as shown in the figure. Several seasonal simulations have been performed to select a configuration for optimal model performance through comparison with



June to August 2003 mean precipitation simulated by WRF-CLM for a U.S. domain at 20 km grid resolution.

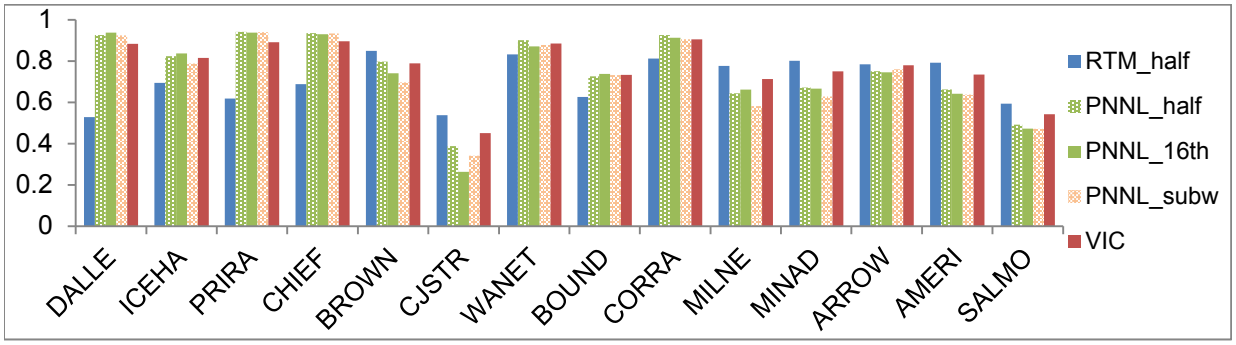
observed data. This U.S. domain will be used to perform long-term simulations for model evaluation and numerical experiments to assess the effects of climate change and land use change.

On development of environmental models, CLM has been selected to provide a consistent modeling framework with for modeling land surface and carbon cycle processes across the global model (CCSM), regional model (WRF), and spatially explicit models that will be coupled with energy infrastructure and operation models. To enhance the capability of CLM for modeling across scales, the soil hydrology component of CLM has been replaced with that of the widely tested macroscale hydrological unit: the Variable Infiltration Capacity (VIC) model. Comparison of CLM-VIC with CLM and observations over flux tower sites and the American River watershed shows that CLM-VIC generally performs better than CLM for vegetation with short roots. Also, CLM-VIC produced more reasonable simulations of subsurface flow, while the simulated subsurface flow produced by CLM often shows high peaks and short recession that are un-characteristics of the slow-varying base flow processes. These results were accepted for publication in the *Journal of Geophysical Research*.

For a more comprehensive evaluation of CLM-VIC, two types of numerical experiments have been designed. First, CLM-VIC has been configured to run over the North American Land Data Assimilation System (NLDAS-2) domain, which covers the conterminous United States and part of Canada and Mexico at 1/8° resolution. Atmospheric forcing data and CLM input data have been prepared to perform long-term integrations from 1979 – 2008. The second type of experiments involve testing CLM and CLM-VIC using the subbasin based approach over the Columbia River Basin (CRB) in the Pacific Northwest. Subbasins have been delineated using Digital Elevation Model (DEM) data to represent the CRB using 5,999 subbasins with an averaged equivalent resolution of 1/8°. A 1-year simulation has been performed and will be expanded to cover 1979–2008 for comparison with the simulation over the regularly gridded NLDAS-2 domain for the same region.

Lastly, a new river routing model has been developed with the goal of providing a more accurate river routing model that supports both grid based and subbasin based implementations of CLM and for coupling with a water management model. The new river routing model (called PNNL model) used a hierarchical river tracing method to construct river networks. The model uses the kinematic wave method to simulate hillslope and subnetwork river routing and the variable storage method for channel routing. Using realistic runoff simulated by the VIC model performed at University of Washington with calibration as inputs, the new river routing model and the River Transport Model (RTM) that is developed for CLM have been used to simulate streamflow over the CRB at 1/2° and 1/16° resolution. The simulated streamflow produced by the new model compares much better with naturalized streamflow than RTM. In addition to applying the new river routing model at regular grids, the model has also been testing using the subbasin approach. Preliminary results show that the model works well with both grid based and subbasin based approach, yielding similar results that are far superior than the RTM for larger river basins where river routing is important for correct simulation of monthly streamflow.

For FY 2012, we plan to: 1) test the irrigation component in CLM, 2) develop a water management model to simulate reservoir operations, 3) couple the water management model with the river routing model, and 4) coupled the water management and river routing models with CLM and perform simulations for model evaluation.



The Nash-Sutcliffe coefficients comparing monthly naturalized streamflow with streamflow simulated by RTM and the PNNL model at different stream gauges. The first bar shows results from RTM at 1/2°; the next two are from the PNNL model at 1/2° and 1/16° resolution using grid based approach; the fourth from the left is from the PNNL model applied to subbasins at an equivalent resolution of 1/16°, and the far right bars are from the U. Washington VIC simulation. From left to right, drainage areas corresponding to the stream gauges decrease in size. River routing is important mainly for river basins with larger drainage areas (those shown on the left).

Development of Regional-Global Climate Assessment Model

Leon E. Clarke, James A. Edmonds, James A. Dirks, Son H. Kim, G. Page Kyle, Marshall A. Wise

◆ This project seeks to create a new and unique modeling capability to explore climate change and climate change responses. It will also result in a regional integrated model that will enable analysis at sub-regional scales (such as states or provinces) in an integrated framework explicitly linked to global-scale phenomena. ◆

This research effort is part of a larger effort to perform climate change integrated assessment at a regional scale. Integrated assessment modeling in the context of climate change is a form of analysis in which all of the relevant human and natural processes are brought into a single computational framework. That is, they combine humans systems such as economic systems, energy systems, and agricultural systems in a single platform with key natural systems such as the climate and the carbon cycle. Although integrated assessment modeling has a long history at the global scale, there is no regional level integrated assessment model or modeling projects. This research effort will build such a regional scale integrated assessment model within the context of a global modeling framework.

This project takes advantage of the fact that PNNL uses the PNNL Global Change Assessment Model (GCAM), an integrated assessment model that combines human systems and natural systems into a single platform for consideration of climate change and climate change response strategies. We are developing a new model based on GCAM which can incorporate sub-regional resolution. This model will be referred to as R-GCAM. We are creating a generic capability, and we are implementing and testing it within one United States sub-region. The development of the generic capability and the testing and implementation in a specific region are taking place simultaneously as interactive processes. The generic capability requires new, innovative coding within the R-GCAM concept, and the testing will require necessary data, along with analysis of model behavior with this new data.

The implementation of this project is based on the completion of two prerequisites, both of which were completed during FY 2010. One critical prerequisite was the completion of a new method of modeling agriculture and land use that is particularly amenable to subregional analysis. The code for this material has been completed and has been successfully tested with preliminary data. The final data set and production of an operating version in GCAM were completed. This required development of consistent data from sources such as FAO and GTAP. These data sources are often inconsistent or limited, so serious data challenges were overcome to create this first version of a spatially resolved agriculture and land use model. The second critical prerequisite is the ability to run GCAM at arbitrary time steps. Prior to FY 2010, GCAM model ran on 15-year time steps. This temporal resolution was based on the long-timeframe generally used for integrated assessment analysis. However, in the context of this larger effort to conduct integrated analysis at a regional scale, fine temporal resolution, particularly in the near-term, is desirable. In addition, the RGCAM model will need to be linked to a range of other modeling tools – for example, a detailed land use model, a detailed regional climate model, and a detailed electricity model – all of which operate at temporal scales well below 15 years. The code and a range of model input developments were completed. The new capability has now been included in the core version of GCAM.

In FY 2011, a fully subregional capability for the modeling building energy was completed, and an exploratory version of a 50-state version of the model was also completed. This 50-state version allows for detailed exploration of building energy in the pilot region as well as the capability to explore building energy consumption in other U.S. regions. The code developed to create the buildings will also facilitate the development of additional subregional sector representations. An important portion of the code development was the reordering of the solution mechanism in GCAM as well as a new, more robust solution algorithm. A subregionally resolved water supply module was also developed in FY 2011. This module will ultimately be coupled with a water demand module to create full water markets in GCAM. The detailed buildings model (BEAMS) was modified in FY 2011 to better allow for changing climate conditions. Efforts have begun to take climate-related data and turn it into necessary inputs for both the R-GCAM and BEAMS.

Activities in FY 2012 will focus on three main areas. The first area is continued development of a water modeling capability within the RGAM framework. Water is a critical input to a range of human and natural systems, including, for example, agricultural systems, and changes in supply from a changing climate will be a critical area of climate impact. The second area is the completion of the regionally resolved buildings sector module in GCAM at the 50-state level. With an existing prototype in place, efforts will focus on building in meaningful scenarios of the future as well as the capability to allow heating and cooling changes to feedback on building energy demands. The third area is the development of the representation of electricity supply and demand at the 50-state level. This will require code development of electricity demands.

Improved Assessment Tool for Offshore Wind Resource Characterization

Zhaoqing Yang, Larry K. Berg, Jerome D. Fast, Taiping Wang, Jennifer C. States, Andrea E. Copping

◆ The overall objective of this study is to improve offshore wind prediction by incorporating the effect of sea state to the sea surface roughness in the Weather Research and Forecasting (WRF) model and to evaluate model uncertainty in order to accelerate development of large-scale offshore wind farms in the United States. ◆

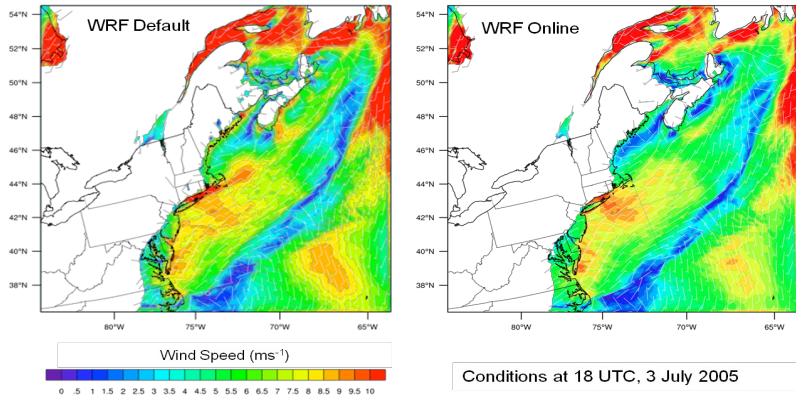
Wind energy is an important component of the Nation's long-term energy strategy. While inland wind resource characterization for wind energy generation is relatively well developed, offshore wind resource characterization and assessment suffers from the uncertainty in model predictions and the paucity of data over large bodies of coastal water. The lack of high density offshore observation networks makes high resolution atmospheric models one of the most important tools for characterizing wind energy potential. The uncertainty in the wind speed prediction at hub-height due to the challenge of proper parameterization of sea surface roughness requires a better understanding of air-sea interaction and improvement of the representation of sea surface roughness. In addition, current offshore wind maps have been generated by AWS Truepower using their proprietary model that is not available to the public, which seriously limits the potential use of the tool by others in the wind power industry and research institutes for further assessment of wind resource in off-shore regions. Use of public domain, open source models leads to transparency in offshore wind resources assessment.

It is thus important to increase the accuracy of wind predictions at hub-height through better representation air-sea interactions using open source community models for resource characterization, environmental impact assessments, and power forecasts under different sea state and wind speed conditions. The current push developing offshore wind resources demands accurate characterization of offshore wind resources using high resolution mesoscale numerical models. The improved representation of wind/wave interactions in numerical models of the atmosphere will enhance our understanding of the air-sea interaction and improve both the prediction of hub-height wind and offshore resource assessment.

In this study, two methodologies are presented: an online wind/wave parameterization within the open-source WRF model and a one-way coupling system utilizing the NOAA operational WaveWatchIII model with WRF. The stand-alone version is based on the hurricane version of the WRF model, which includes parameterizations for very large wind speeds and a simple ocean model to account for the impact of precipitation on the sea-surface temperature. We have replaced the surface roughness parameterizations in that version of WRF with relationships based on the wave height, wave length, and fetch that are optimized for smaller wind speeds that are more appropriate for offshore wind energy applications. In the wind/wave coupling approach, we have estimated the sea surface roughness height using wave climate parameters calculated by the WaveWatchIII model.

These modeling systems have been tested for periods over the Gulf of Maine observed during the International Consortium for Atmospheric Research on Transport and Transformation in July 2004, which included the deployment of a number of wind profiling radars near the New England coast or on small islands, the NOAA Research Vessel Ron Brown, and data collected from the Gulf of Maine Ocean Observing System in July 2004 and 2005.

The main findings of this study are: 1) existing treatment of wind/wave interaction in WRF is crude and inadequate for offshore wind energy applications, 2) two alternative methodologies (i.e., online parameterization and one-way coupling with an operational wave model) are proposed and implemented in WRF to improve wind/wave interactions, 3) sea surface roughness estimated based on operational wave model outputs shows strong temporal and spatial variations, which are critical to wind speed predictions at hub-height, and 4) model results show improved sensitivity of wind speed within the planetary boundary layer to wave characteristics.



There are significant differences in predicted wind speeds at hub-height between the WRF default and online wind/wave parameterizations. The online coupling approach leads to generally smaller wind speeds at hub-height. Similar results are obtained for one-way coupling with the operational wave model approach.

Improving the Characterization of Aerosols as Forcing Agents in the Climate System

Philip J. Rasch, Vinoj Velu, Dilip Ganguly, Nathaniel Beagley, Hailong Wang

◆ The focus of this project is on understanding how the improvements to representation of aerosol and cloud processes manifest themselves in a fully coupled climate model, and how aerosols influence precipitation and associated dynamical features of monsoons. ◆

Virtually all assessments of climate change have identified aerosols as among the most uncertain of forcing agents and very important to climate. Aerosols are strongly influenced by anthropogenic activity, and it is important to produce an accurate representation in climate models to understand how mankind is influencing climate. With a long history of producing fundamental research involving aerosols, PNNL has generally focused on a process level understanding but has not attempted to determine the climate response, particularly at the global scale.

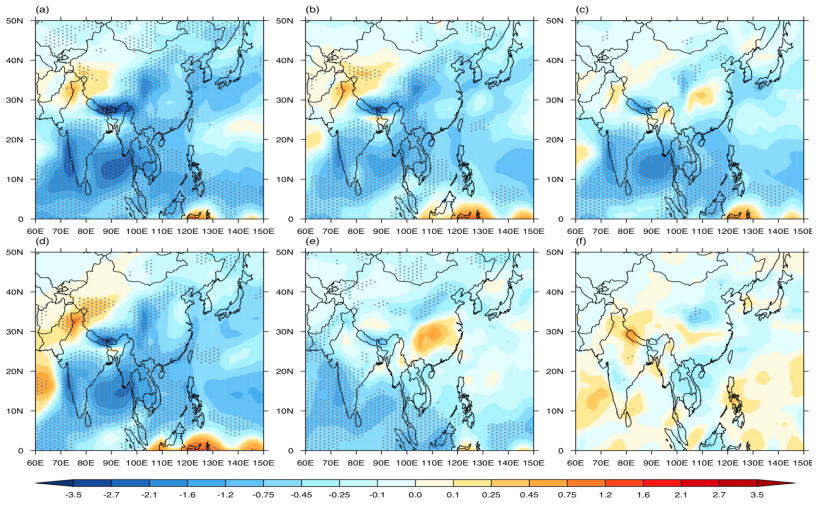
This project was designed to strengthen PNNL contributions by understanding responses to climate forcing, examining how the improvements derived using field programs and detailed model frameworks influence the model climate and altering the projections of climate change at the global scale. The project contributes to answering the scientific questions regarding how aerosols influence fundamental circulation features of the climate system such as monsoon circulations, and how have changes in aerosol emissions due to mankind changed monsoon circulations.

Our goal was to explore the role of certain aspects of aerosols important to climate change in the Community Earth System Model (CESM), a national tool, with a focus on identifying mechanisms involving aerosols and climate feedbacks This work builds on PNNL's capabilities by exploring responses to climate forcing, and examines how the process-level improvements produced using field programs and more detailed model frameworks influence the model climate, changing forcing/response patterns, and projections of climate change at the global scale.

Prior to the current fiscal year, we examined the thermal, radiative, and hydrological responses to the direct, indirect, and semi-direct effects of anthropogenic fossil fuel and biomass burning aerosols and interactions with natural (i.e., dust and sea-salt) aerosols on Asian and African monsoon systems using a variety of CESM configurations. We systematically removed or constrained emissions (by sector and geographic region) of aerosol species and precursors to identify the model response to these emissions and compared these changes to historical changes in precipitation, cloudiness and temperature.

In early 2010, the first satisfactory coupled simulations were demonstrated, which are capable of producing information close to the historical record of surface temperature changes over the globe. The simulations show a reasonable estimate for many climatic features for the last few decades, including distributions of precipitation, El Niño/La Niña-southern oscillation, cloud radiative forcing, aerosol concentrations, and aerosol forcing. The model was officially released in July 2010.

Our results suggest that the anthropogenic aerosols cool the atmosphere over land and the northern Indian Ocean, stabilizing the atmosphere and weakening the south Asian summer monsoon by slowing down the Hadley circulation. Changes in cloud fraction induced by these aerosols are an important driving factor contributing to this slow down. Anthropogenic aerosols cause a reduction in mean summer monsoon precipitation rate over most parts of the Indian subcontinent with maximum reduction along the western coastline of the Indian peninsula and eastern Nepal. We also found that aerosols from fossil fuels and biomass-burning contribute



June-July-August-September precipitation anomaly (mm/day) due to anthropogenic aerosols from a) the globe, b) fossil fuel only, c) biomass burning only, d) the Asia domain, e) the globe except for the Asia domain, and f) global BC alone. Stipples represent areas where the anomalies are at or higher than 95% confidence level based on student's t-test.

almost equally to the total reduction in rainfall over India. Similarly, over North Africa, biomass-burning aerosols can significantly reduce local rainfall through both light-absorbing and microphysical effects that modulate modeled cloud fraction, radiation budgets, and low-level circulation patterns.

While the precipitation response is driven primarily by local forcing, regional surface temperature changes over Asia are more strongly influenced by the anthropogenic aerosols emissions occurring further away (non-local changes). Resulting circulation changes oppose the prevailing low-level and the upper tropospheric winds over the northern Indian sub-continent. We found that the feedbacks associated with changes in sea surface temperature (SST) and sea ice distributions play an important role in the full climate response due to anthropogenic aerosols. Precipitation and land temperature changes are quite different when SSTs are not allowed to respond.

Using satellite observations of precipitation and aerosol optical depth along with CESM, we discovered that natural aerosols play an important role in modulating the Indian monsoon precipitation and its response to anthropogenic aerosols. Dust and sea-salt play differing roles in modulating anthropogenic impacts on precipitation and, in fact, tend to oppose each other. We found that sea-salt aerosols tend to reduce the precipitation efficiency of clouds over ocean and subsequent increase over the Indian land mass. Our study also suggests that the natural aerosols have an important role in monsoon precipitation and may alter the anthropogenic impacts.

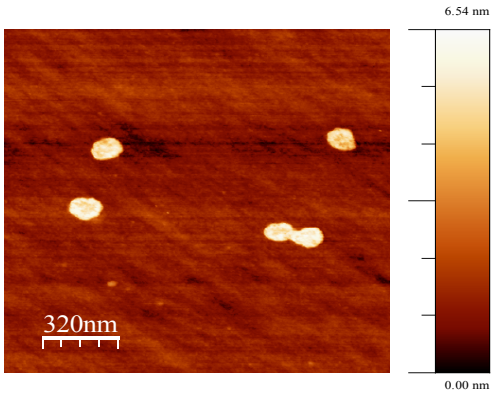
We have three journal articles in preparation on these topics and have presented this work at national and international meetings.

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

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

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

Storage of anthropogenic CO_2 in deep underground saline aquifers is a viable method to slow CO_2 increase in the earth's atmosphere while allowing the use of fossil C-based fuels. In these aquifers, CO_2 will exist in a supercritical (sc) state. Consequently, numerous studies measure the thermodynamic and kinetic properties of the reactions that would occur for various mineral systems in the presence of hydrous $scCO_2$. Site-specific reactions occurring at these points are entirely unknown and sum to produce the interfacial phenomena observed in bulk studies, described macroscopically by equilibrium thermodynamics or kinetic rate laws. To understand and control these chemistry interfaces necessary to assess the practicality of subsurface carbon sequestration, a quantitative understanding of these fundamental interactions is required. To address these issues, we are building an atomic-force microscope capable of operating at the high pressures and elevated temperatures that are expected in these underground locations. This capability will be the first of its kind to operate in CO_2 and water-dominant $scCO_2$ water phases where dehydration, mineral trapping, and solubility trapping reactions relevant to carbon sequestration occur. We will demonstrate use of this capability to study interfacial aspects of silicate dissolution and carbonation chemistry under supercritical conditions.



Formation of ~150nm diameter precipitates on the surface of forsterite upon 2-hr reaction with water saturated $scCO_2$ at 90 bar and 35°C.

In FY 2009, we manufactured a high pressure test cell with a multimode hydrothermal atomic force microscope (AFM) head modified to accommodate the test cell. Connections were made in the cell permit inlet and outlet ports for the $scCO_2$ and introduced a K-type thermocouple for the measurement of temperature within the test cell for noise measurements. Proceeding to FY 2010, we built an AFM head capable of operating at pressures up to 100 bar and interfaced it with a commercial AFM controller and $scCO_2$ delivery system for a fully functional high pressure AFM head. Under target conditions of 80 bar, the AFM head imaged single atomic steps on the surface of calcite in a nitrogen environment. This is the first time any AFM demonstrated atomic-scale imaging at these pressures. This indicates that this system should be capable of imaging mineral surfaces under $scCO_2$.

In FY 2011, we began imaging mineral surfaces in $scCO_2$. Images of a freshly cleaved, model calcite (1014) surface in anhydrous $scCO_2$ at 35°C and 100 bar show 3.2Å monatomic steps that remain static over the course of the experiment, demonstrating that calcite is unreactive to dry $scCO_2$. Conversely, calcite exposed to air for 20 hrs prior to imaging shows a ~1.2 nm film that disappears during the experiment when anhydrous $scCO_2$ at 35°C and 80 bar passes over the surface. These images not only demonstrate the ability of the high pressure AFM to obtain dynamic in situ data on mineral surfaces but are also consistent with previous work that shows a 1.5-nm hydrated calcium carbonate layer in ambient conditions using polarization force microscopy.

Mineral transformation of forsterite in water saturated $scCO_2$ was investigated at 90 bar and temperatures of 35°C and 50°C. The figure shows the formation of precipitates on the surface of the forsterite under these conditions at 35°C. Subsequent XRD analysis does not show a secondary phase, indicating either the precipitate is amorphous or the density is too low to be detected. The high pressure AFM can also detect the formation of water films in $scCO_2$ on the surface of forsterite through collection of force-distance data. The presence of a water layer, assumed essential for the rapid transformation of forsterite to magnesite, would manifest itself as a large adhesive force upon retraction of the AFM tip from the surface. We observed a substantial adhesive force in a water-saturated $scCO_2$ fluid not present in anhydrous $scCO_2$, indicating that a water film is likely present on the forsterite surface under those conditions.

Also during FY 2011, we enhanced the fluid delivery system, adding a second high pressure syringe pump and a high pressure reactor. These additions allow for more precise control of the composition of the $scCO_2$ enabling the high pressure AFM to operate at targeted water saturation conditions.

Integrated Regional Earth System Model (iRESM) Prototype Regional Testbed Specification and Selection

Lai-Yung (Ruby) Leung

◆ The development and testing of new systems through modeling frameworks and tools that integrate climate with hydrology, land systems, socio-economics, and energy at the regional scale enable the evaluation of regional feedbacks and interactions between energy, hydrology, climate, biogeochemistry, and global implications of socioeconomic processes. This project aims to execute a systematic approach to developing testbeds studies to demonstrate and evaluate the unique capabilities of the integrated regional earth system models (iRESMs). ◆

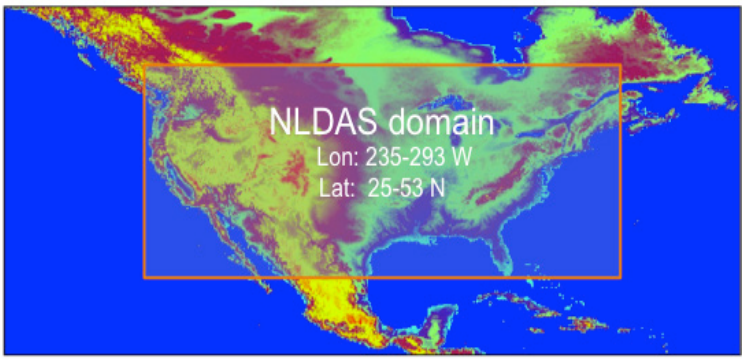
An important component of any modeling activity is evaluation or validation. Establishing a robust evaluation process through careful and systematic specification and the selection of testbeds or pilot studies are of vital importance to ensure that the model evaluation can improve the understanding and quantification of key model biases and uncertainties and to provide insights for model improvements. Four types of scientific approaches have been developed and applied to evaluate and understand model behaviors and sensitivities:

- *Hindcast experiments*, where models are evaluated on their skill in reproducing the historical conditions and the associated spatial and temporal variability
- *Analysis and diagnostics of model simulations*, to attribute the sources of model errors
- *Sensitivity experiments*, to understand the impacts of model parameterizations, model feedback processes, or the effects of external perturbations
- *Model intercomparison*, to assess model biases and uncertainties under a common set of simulation conditions.

This project will develop and execute a systematic process to select the iRESM regional testbed that will be used to evaluate the iRESM model and its components. This includes developing a focused set of science questions or hypotheses to be addressed by the iRESM, developing the scientific approach for model testing and evaluation, selecting geographic regions and time periods, developing the testbed database, and developing evaluation metrics. The prototype iRESM testbeds will highlight the interactions between the natural systems and energy, water, and land use.

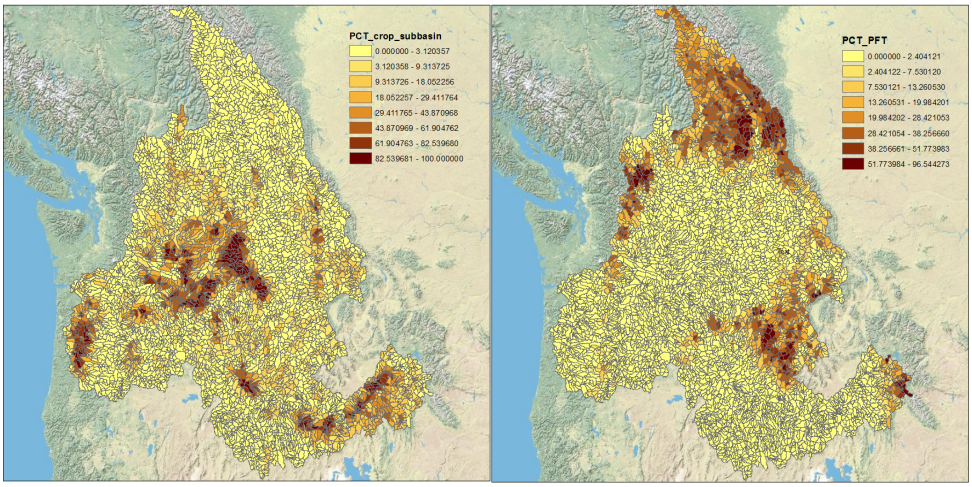
In FY 2010, the team adopted the region definition used in the U.S. National Assessment, which divides the conterminous states into Northwest, Southwest, Great Plains, Midwest, Northeast, and Southeast. The Midwest emerged as the region of choice for the first pilot study because it represents significant interactions among climate, land use, energy, and water. Next, we developed a database that supported modeling of the pilot region, including data for energy infrastructure and hydrologic modeling. Finally, we began to map a strategy for model evaluation and uncertainty characterization.

During FY 2011, a coordinated framework for evaluating the iRESM models was developed. The framework includes performing and evaluating numerical simulations in three different phases. In Phase 1, individual models are evaluated in a hindcast mode with each model driven by observed conditions. In Phase 2, some models with one-way coupling will be evaluated. In Phase 3, some two-way coupled models will be evaluated. Progress has been made toward the first phase model evaluation. The North American Land Data Assimilation System (NLDAS-2) has been selected to provide atmospheric forcing data for driving all the individual models, including building energy model, electricity infrastructure model, crop model, and hydrology model. The NLDAS-2 atmospheric forcing data covers the conterminous United States and parts of Canada and Mexico at 1/8° resolution. The forcing data has been expanded to include a larger area that covers the same region of the RESM domain. To prepare for the Phase 1 evaluation, each modeling team has been preparing datasets that are needed as model inputs or for model evaluation. For RESM, boundary conditions for WRF are being developed for simulating the regional climate of the U.S. for 30 years (1979–2008).



The NLDAS-2 domain (box) and expanded NLDAS-2 domain (whole area) where atmospheric forcing data has been prepared for driving offline models such as CLM and EPIC for the Phase 1 evaluation.

The NLDAS-2 forcing data will be used to run CLM at 1/8° resolution. To construct input data to evaluate CLM in a sub- basin approach, watershed boundaries, river network, and vegetation data has been prepared for the Columbia River Basin. These include using the HydroSHED global 90 m Digital Elevation Model (DEM) data and 15 arcsec river networks to construct river networks. To delineate watershed boundaries and river network, the ArcSWAT data is used. MODIS land cover data at 500 m resolution and other surface parameters at 1 km resolution are used. Shown below some examples of CLM input data for the Columbia River Basin. The same datasets and methods will be used to configure the model for the Midwest pilot region.



Percentage of crop (left) and needleleaf evergreen temperate forest in the Columbia River Basin based on MODIS data processed for about 6,000 subbasins delineated using HydroSHED data for an equivalent spatial resolution of 1/8°.

The EPIC crop model has been configured to run at 60 m resolution using the NLDAS-2 atmospheric forcing. Other EPIC input data such as soil data and land use history has also been prepared by processing the SSURGO and Crop Data Layer (CDL) data.

For energy modeling, significant progress has been made to develop data for siting of new energy infrastructure and modeling electricity operations. This includes procurement, development, processing, and analysis of various GIS data layers. Some of the challenges in data development include transformation of different data into a common, open standard storage format that balances storage footprint with performance, compositing of data from multiple sources that lack continuous, contiguous national coverage, upscaling and downscaling of data layers to a common grid, and handling of huge file sizes that require custom 64-bit geoprocessing routines to manage memory for complex tasks. The energy models will also be evaluated using a hindcast mode, but unlike RESM, CLM, and EPIC, which will simulate 30 years, energy simulations will be performed only for two time periods corresponding to a historical and the present conditions. Corresponding input data such as building stocks is being developed to support the simulations.

For FY 2012, each modeling team will complete data development for the Phase 1 evaluation, and begin performing the simulations outlined above. The simulations will be analyzed and compared against observations to assess model skills in simulating climate (RESM), hydrology and water supply (CLM), crop yield (EPIC), and building energy demand (BEND), energy infrastructure siting (SITE) and electricity operations (EOM).

Micromodel Pore-Scale Studies of Caprock-Sealing Efficiency and Trapping Mechanisms Related to CO_2 Sequestration

Martinus Oostrom, Jay W. Grate, Changyong Zhang

◆ To improve our understanding of subsurface supercritical carbon dioxide ($scCO_2$) storage and caprock sealing efficiency, we are conducting pore-scale experimental and numerical studies of processes related to caprock-sealing efficiency and trapping. Research at the pore scale is an essential first step to facilitate upscaling of fluid displacement processes to the field injections. ◆

Geological storage of CO_2 is considered in deep saline aquifers, depleted oil and gas reservoirs, and unminable coal beds. For the first two options, interactions at fluid-fluid and fluid-mineral interfaces (such as capillarity, mass transfer, interfacial tension, and wettability) greatly influence fluid displacement in porous media. Two of the main issues related to any subsurface sequestration project are the potential leakage of $scCO_2$ out of the reservoir into the caprock, followed by transport into the atmosphere and the storage capacity of the reservoir rock. The integrity of the overlying caprock and the storage capacity of $scCO_2$ in deep saline aquifers or reservoirs are affected by interfacial interactions. Both caprock-sealing efficiency and free-phase $scCO_2$ trapping are to a large extent determined by porous medium properties (e.g., pore geometry, grain size and distribution), fluid properties (e.g., density, viscosity, interfacial tension), and porous medium-fluid interactions (e.g., wettability) occurring at the pore-scale. Data related to interfacial interactions are scarce, and knowledge of displacement of brine by $scCO_2$ (main drainage) and vice versa (imbibition) under various wettability conditions is limited.

To improve our understanding of subsurface $scCO_2$ storage, pore-scale experimental and numerical studies of processes related to caprock-sealing efficiency and trapping are needed. The caprock-sealing efficiency is a measure of the capillary pressure at the caprock: reservoir interface that needs to be exceeded before $scCO_2$ can move into the caprock. The major trapping mechanisms include storage of free-phase gas through hydrodynamic and capillary trapping, dissolution in formation brines, and mineral trapping through geochemical reactions. Of these trapping mechanisms at the reservoir scale, hydrodynamic and capillary trapping processes may occur on much smaller timescales than mineral and dissolution trapping.

In this project, we will complete a series of micromodel experiments at supercritical conditions while addressing the following scientific challenges:

- identify roles that porous medium properties, fluid properties, and wettability (including contact angle hysteresis) play during hydrodynamic (primary) trapping, when $scCO_2$ displaces brine, and during capillary (secondary) trapping when brine displaces $scCO_2$
- examine the effects of fluid-fluid interfacial tension, pore-size geometry, and wettability on caprock-sealing efficiency
- study and understand the relationships between capillary pressure, fluid saturation, relative permeability during pore-scale displacement processes.

To address these challenges, we designed and constructed unique high-pressure systems for micromodel experimentation and a capability to obtain interfacial tension and contact angle data at supercritical conditions. We have developed to modify micromodel wettability and improve displacement visualization using solvatochromic dyes. Displacement experiments have been conducted under high pressures and temperatures typically found under reservoir conditions.

In FY 2010, we developed a novel method to distinguish between competing fluids at the pore-scale using solvatochromic dye. The use of Nile Red with imaging methods facilitates visualization of phase identity at specific locations; the interfaces between the two immiscible liquid phases; wetting behavior of the wetting phase within the porous structure; and retention of the wetting phase as thin films around pillars and as bridges across the pore throats. We demonstrated the ability to investigate CO_2-related chemistry issues at the micromodel scale. Our experiments showed that mineral precipitation along CO_2 plume margins may affect injection and sealing efficiency. Another important accomplishment was completing a series of micromodel displacement experiments to investigate the impacts of viscous and capillary forces on fluid distribution in a silicon-based homogeneous pore network micromodel. Results showed two distinctive fingering mechanisms – viscous and capillary – associated with viscosity ratio at low capillary number. Other results revealed a linear correlation between interfacial area and nonwetting fluid saturation.

During FY 2011, we identified Cumarin 153 as a solvatochromic dye for use under supercritical conditions as it facilitates visualization of phase saturations at specific locations and interfaces between two immiscible liquid phases. The discovery for this purpose was based on a novel method developed in FY 2010 using these types of dyes to

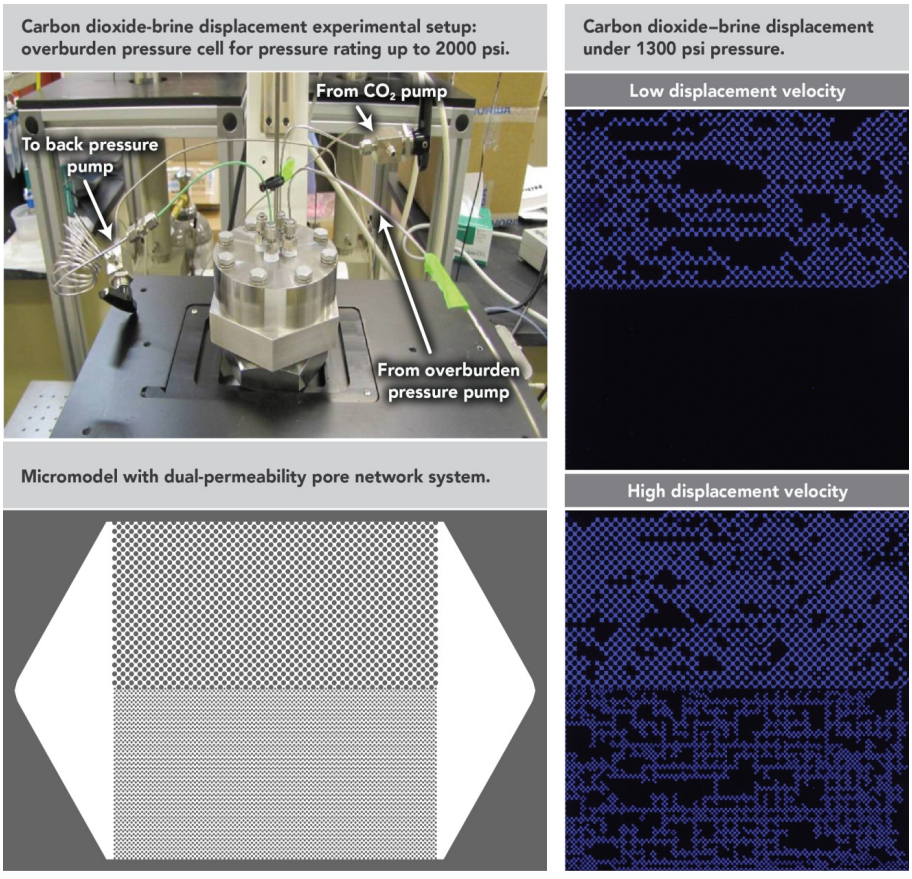
distinguish between competing fluids at the pore-scale under ambient conditions. A description of this novel technique was published in *Water Resources Research*.

The micromodel experiments at high-pressure injection conditions conducted in FY 2011 were conducted with a newly designed and constructed high-pressure cell equipped with high quality syringe pumps for accurate and precise fluid injections at constant pressure or at constant injection rate. Full control of either boundary pressure and injection rate is needed to understand observed phenomena and for modeling purposes. The design of the new pressure cell allows for fluid displacement visualization using epifluorescent microscopy equipped with charge-coupled device camera and/or hyperspectral cameras. The temperature of the system is controlled within 0.1°C up to 60°C.

We used the new high-pressure apparatus in FY 2011 to conduct liquid CO_2–water displacements in a pore network micromodel with high and low permeability zones. Recently published in *Environmental Science & Technology*, this work is important, as permeability contrasts exist in multilayer geological formations under consideration for carbon sequestration. Due to the low viscosity ratio, unstable displacement occurred at all injection rates over two orders of magnitude. Liquid CO_2 displaced water only in the high permeability zone at low injection rates, with the mechanism shifting from capillary fingering to viscous fingering with increasing flow rate. At high injection rates, the CO_2 displaced water in the low permeability zone with capillary fingering as the dominant mechanism. A continuum-scale two-phase flow model with independently obtained input parameters was used to predict CO_2 saturations in the dual-permeability field, and a reasonable agreement with the micromodel experiments was obtained for low injection rates. However, the continuum-scale model does not account for the unstable fingering processes observed at higher rates and hence tends to overestimate CO_2 saturations when viscous fingering occurs.

In our final FY 2011 accomplishment, we developed and tested new methods to change the wettability of initial water-wet micromodels to oil wettability using treatment with silanes. An analysis of treated micromodels indicated a contact angle change from less than 30 degrees to greater than 150 after applying the alteration method. This work provides a benchmark evaluation of surface wettability alteration by the silanization method, and demonstrates a linear correlation between the resulting measured air-water and oil-water contact angles. This methodology can be applied to studies of immiscible fluid displacement across scales with applications to important systems including geologic carbon dioxide sequestration, enhanced oil recovery, and nonaqueous phase liquid migration in the subsurface. We have shown how to obtain a full range of wettabilities on silica surfaces using silanization methods, including the identification of specific silanes to obtain intermediate wet surfaces. These studies on wettability alteration are being carried out in conjunction with fundamental studies of immiscible fluid displacements and studies at high pressures with liquid and $scCO_2$ in microfabricated pore network micromodels.

In FY 2012, we will develop methods to create different wettability zones in one micromodel. The goal is to manufacture both models that have two distinct wettability zones such as a water-wet zone representing the reservoir and an intermediate-wet zone representing the caprock. Micromodel experiments will be conducted to study hydrodynamic trapping mechanisms and caprock-sealing efficiency. A pore-scale model developed in another project will be used to design the micromodel experiments, and we will use the obtained experimental data to test and verify the numerical model.



A new high-pressure cell has been developed to visualize displacement of brine by $scCO_2$ in micromodels. Initial results show large differences in displacement, depending on CO_2 injection rate.

Predicting Climate Change Impacts on Hydropower and Riverine Ecosystems

Timothy P. Hanrahan, Marshall C. Richmond, Mark S. Wigmosta

◆ The future management of water resources for hydropower production in the Columbia River Basin and around the world requires attention to long-term implications of climate change. The purpose of this project is to develop heightened scientific understanding and improved analytical tools to enhance the predictive capability of climate change effects on hydropower production and riverine ecosystems. ◆

Recent assessments of climate change impacts on the aquatic environment have been limited to large, spatial-scale predictions of future hydrologic and temperature regimes and the subsequent general ecological effects on a selected group of organisms. For example, *The Washington Climate Change Impact Assessment* evaluated future hydrologic and temperature changes across the entire Columbia River Basin, and the subsequent impacts to the aquatic environment were limited in scope to evaluating the habitats of salmon as a group and not individual species. Not only was this assessment on the aquatic environment simplistic in its scope, but also the fundamental methods used for predicting stream temperature changes were based on simple statistical regression rather than physics- and process-based models.

We require a better predictive capability of climate change effects on hydropower production and riverine ecosystems to improve the information available to water management decision makers and the public policy and planning officials responsible for integrating this information into social and economic forums. Using the Columbia River Basin as an example, decisions on water management in the system (e.g., timing, frequency, magnitude, duration of reservoir releases) will vary significantly depending on the predicted riverine ecosystem impacts of climate change. This project will provide a scalable, physics-based hybrid modeling system to understand and evaluate measures to mitigate the environmental impacts of climate change on hydropower production, water resources management, and riverine ecosystems in the greater Columbia River Basin, both under current and future climate conditions.

We are developing a system by linking a set of well-established models that simulate watershed hydrology, reservoir and river hydrodynamics, water quality, and ecosystem processes. During FY 2010, the models were integrated and applied to a test watershed, the North Fork Clearwater River Basin, including Dworshak Dam and Reservoir. Project efforts were focused on model development, linkage, and testing.

Model development during FY 2011 included revisions to the watershed hydrology and stream channel models. These revisions were completed to provide better approximations of land surface energy exchange affecting stream channel water temperature and better linkages between models. The Distributed Hydrology Soil Vegetation Model (DHSVM) was enhanced and modified to output text files of channel segment meteorological conditions and inflow estimates which are then used by the one-dimensional Modular Aquatic Simulation System (MASS1) model for channel routing and stream temperature simulation. DHSVM was modified to output the topology of the stream channel network as required for MASS1 input. Below-canopy estimates of meteorological conditions (e.g., attenuated wind speed, solar radiation, etc.) were also supplied in the proper format for each channel segment along with surface and subsurface inflow.

Historic climate data and predictions of future climate scenarios were compiled for the North Fork Clearwater River Basin in order to provide temperature and precipitation input to simulate watershed hydrology. DHSVM was set up to model the water cycle dynamics within the study watershed. Daily average streamflow and water temperature were modeled for the existing and future climate conditions. Simulated streamflow and temperature were used as input for modeling the hydrodynamics and water quality in Dworshak Reservoir and downstream of Dworshak Dam.

Hydrodynamics and water quality were modeled with the two-dimensional model CE-QUAL-W2. Digital elevation models (DEM) for the river channels and reservoir were developed. Empirical data for model calibration and validation were acquired for locations throughout Dworshak Reservoir. The completed model setup was used to simulate multiple water quality parameters for several different years. Model estimates for the vertical profile of temperature and dissolved oxygen showed good agreement with empirical measurements.

This project resulted in the development of a prototype modeling system for integrated predictions of climate change impacts on watershed hydrology, reservoir water quality, and river ecosystems. Applying this modeling system within the framework of the associated conceptual model for hydropower operations and environmental mitigation strategies will foster better predictions of climate change impacts on hydropower and riverine ecosystems.

Predicting the Feasibility of Geologic Co-Sequestration of CO_2, SO_x and NO_x Under a Broad Range of Conditions

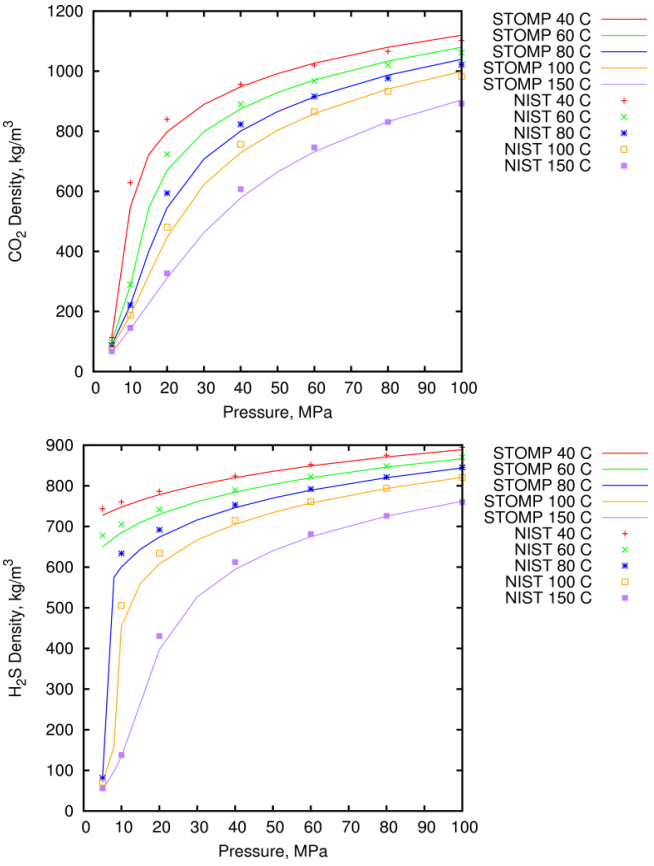
Diana H. Bacon, Ramya Ramanathan, Mark D. White

◆ Using the mineralogy of deep saline systems to co-sequester NO_x and SO_x along with CO_2 could significantly lower the cost of retrofitting coal-fired power plants for carbon sequestration. We aim to develop a simulator that will improve predictions of the impact of geologic co-sequestration of CO_2, NO_x, and SO_x on target formation and caprock hydraulic properties under a broad range of mineralogical and phase conditions. ◆

Due to limitations of previous simulators in handling the injection of multi-component and multi-phase mixtures, previous modeling studies of co-injection of SO_2 with supercritical (sc)CO_2 have either simplified hydrogeological systems or have already dissolved in an aqueous phase rather than acted as constituents of the non-aqueous phase. The opposite (and equally unrealistic) extreme case is a scenario in which SO_2 is limited by diffusion through a stationary scCO_2 phase. A better method is to simulate the injection of sc/gas mixtures, but a combined component/phase mixture approach is lacking, along with few modeling studies on the impacts of NO_x co-sequestration.

This project aims to improve predictions of the impact of geologic co-sequestration of CO_2, NO_x and SO_x on target formation and caprock hydraulic properties under a broad range of mineralogical and phase conditions. Numerical simulation of CO_2, SO_x, and NO_x co-sequestrationinto deep geologic reservoirs requires modeling complex, coupled hydrologic, chemical, and thermal processes, including multi-component, multi-fluid flow and transport, and chemical interactions with aqueous fluids and rock minerals. Our work will develop a three-phase variable component nonisothermal simulator capable of mimicking the geological sequestration of a mixture of gases in deep saline and depleted oil and natural gas reservoirs. The new simulator that incorporates these complex processes will be used for a survey of the effects of co-sequestration under a wide range of reservoir hydrogeochemical conditions. The results of the modeling survey will help identify the range of reservoir conditions under which co-sequestration is feasible and will guide future studies involving micromodel pore-scale experiments with mineral substrates and mixtures of CO_2, SO_x, and NO_x.

To determine the geologic scenarios where co-equestration is practical, we began in FY 2010 by calculating the carbon sequestration and co-sequestration potential of 150 minerals to use as a guide for future simulations. Geochemical simulations indicated that co-injection of CO_2 and SO_2 resulted in SO_2 mineral sequestration. The amounts sequestered were greater and more persistent in dolomite and basalt than in glauconitic sandstone. After 5,000 years, 87 to 0 percent of the SO_2 remains sequestered in the glauconitic sandstone. In all cases, co-injection of 1 percent SO_2 with CO_2 did not appreciably reduce the amount of CO_2 sequestered nor did it induce a measureable change in porosity versus injection of CO_2 alone.



Predicted density of CO_2 and H_2S over a wide range of conditions.

In FY 2011, we focused on building numerical simulation capabilities for geologically sequestering a mixture of gases in deep saline and natural gas reservoirs. We developed the new two-phase, nonisothermal, multi-component operational mode for the PNNL-developed STOMP simulator. The new operational mode has been founded on the premise that each phase will have variable compositions and component numbers. Phase and component flexibility has been handled numerically through implementation of the Peng-Robinson cubic equation of state with a two-phase flash equilibrium model, where phase composition is defined through fugacity equilibria. The new equation has been written so that a general number of co-contaminants may be specified and is

not limited to NO_x and SO_x. This allows the simulation of co-sequestration of Hg and other co-contaminants as well as other flue gases such as O_2.

The predictions of the new Peng-Robinson equation of state in STOMP for component density, viscosity, enthalpy have been compared with the results reported for CO_2 and H_2S by the National Institute of Standards and Testing (NIST). Predictions of the solubility of CO_2 and H_2S in pure water and brines have been compared to experimental results. The new simulator has been extensively tested to ensure that calculations of internal and boundary fluxes are correct for perturbations of all primary variables, including temperature, aqueous and non-aqueous pressure, non-condensable gas component mole fraction, and salinity under both single-phase and two-phase conditions. We also developed a kinetic geochemical model of hematite dissolution experiments in CO_2, SO_2 and brine in collaboration with the National Carbon Institute in Spain applicable to co-sequestration in redbeds.

In the coming fiscal year, we will be adding the capability to link geochemical reactions with formation minerals to each component to simulate the impact on formation storage capacity due to changes in porosity. Also, we will be implementing fully coupled well models to avoid solution instabilities and improve computational efficiency. We will prepare journal articles detailing the development and validation of the new equation of state against experimental data, and application of the new model to field scale simulations of co-sequestration in various formations such as sandstone, dolomite, basalt and redbeds. Ultimately, we hope to implement a parallel solution scheme using global arrays , which is capable of scaling to 130,000 processors.

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

Philip J. Rasch, Jerome D. Fast, William I. Gustafson Jr., Baldwinder Singh, Richard C. Easter

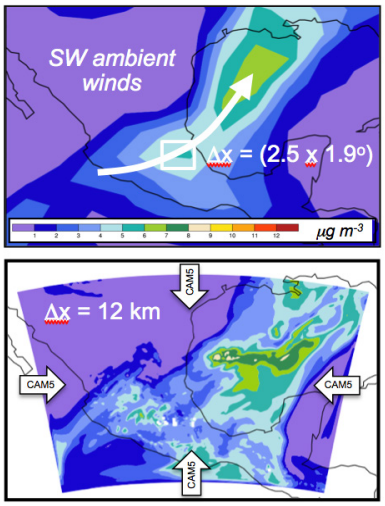
◆ The goal of this project is to compare the treatments for processes used in global climate models with those commonly used in cloud/mesoscale models and enable a systematic, consistent methodology to evaluate various treatments of physics, chemistry, and feedback processes for both models that will help improve both model classes. ◆

Global climate models (GCMs) are tools used to explore interactions between complex processes governing the evolution of the earth's climate and assist in understanding and projecting climate change. They are incomplete and require many approximations to be affordable. By comparison, regional models (RMs) use fewer approximations and more elaborate representations for processes because they simulate features for shorter time scales over smaller regions. The RM treatments use small cell sizes and costly representations that are too expensive to be routinely used for global models. Thus, the two communities represent atmospheric processes differently.

This project produced a modeling framework that allows treatments for the processes used in GCMs to be compared with those commonly used in cloud and mesoscale models and developed a systematic, consistent methodology to evaluate those formulations. We studied a single suite of physical parameterizations (radiative transfer, convection, turbulent boundary layer, aerosols, cloud microphysics) in both GCM and RM. We then transferred representations of physical processes from the Community Atmospheric Model (CAM) to the Weather Research and Forecasting (WRF) model and produced an initial evaluation of this suite in WRF at higher spatial resolution. This provides an opportunity to compare the more costly, elaborate parameterizations commonly used in regional models and cloud models with those in GCMs. Cost and benefits of treatments can be explored, producing a synergy in modeling activities for weather and climate. Adding the suite of physical representations from CAM to WRF helps separate sensitivity of solutions to spatial resolution from complexity in process representation.

In FY 2010, we completed integration of the cumulus, shallow convection, microphysics, boundary layer, and aerosol schemes from CAM to WRF, including the climate feedback processes associated with coupling aerosols with radiation and clouds. A simplified version of the CAM-Chem chemistry was integrated but is not yet coupled with aerosols. A methodology was established for coupling the codes to WRF that leaves the original CAM modules largely untouched so that future CAM updates can be easily transferred to WRF without significant reprogramming. We discussed and solicited input regarding software engineering strategies and goals with the relevant National Center for Atmospheric Research global and mesoscale communities and gave presentations at the CAM and WRF workshops for acceptance. Portions of our code were released in the public version of WRF in April 2011.

Also during FY 2011, we compared the CAM aerosol formulation with two more complex aerosol schemes using the same emissions, meteorology, trace gas chemistry, and initial and boundary conditions using the Aerosol Modeling Testbed methodology. While the CAM aerosol scheme is fastest computationally, we identified areas for improvement, particularly in CAM's treatment of secondary organic aerosols (SOA). In the vicinity of large anthropogenic emissions, SOAs were too large to be compared with measurements and other aerosol schemes. We are testing new treatments of SOA formation at high spatial resolution in WRF before exploring their consequences at the global scale in CAM. This is one example where treatments of climate-relevant processes can be evaluated and improved.



Comparison of particulate matter predicted by CAM (top) and WRF (bottom), demonstrating the differences associated with spatial resolution. The smaller grid spacing in WRF leads to additional spatial variability that is more realistic when compared to observations.

As part of testing the new modeling framework, we evaluated simulations using data collected over the central U.S., Mexico, and Alaska. We developed better tools for using CAM output as initial and boundary conditions for WRF. The outcome of this work enables new types of climate research for the development of parameterizations for aerosols, clouds, and their interactions as well as and scale-dependency of climate processes to be proposed as new projects and from which two journal articles are being prepared.

Uncertainty Quantification and Risk Assessment Pipeline for Carbon Sequestration

Guang Lin, Paul W. Eslinger, David W. Engel, Zhangshuan Hou, Jian Lin, Yilin Fang

◆ Motivated by the challenges of uncertainty in geological carbon sequestration modeling and simulations, this project aims to develop an uncertainty quantification and risk assessment pipeline for carbon sequestration to improve the predictive modeling capability for geological carbon sequestration simulators. ◆

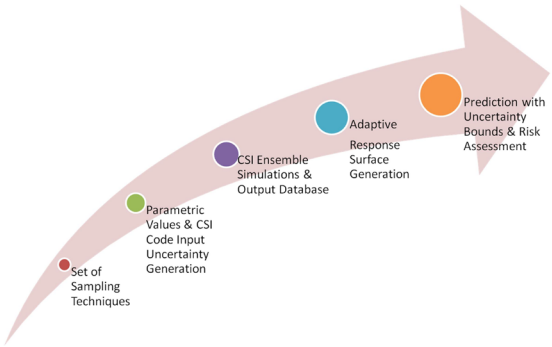
With worldwide energy efficiency improvements underway, fossil fuel usage, a major source of atmospheric emissions of CO_2, will continue to provide the dominant portion of total energy in the world. CO_2 capture and storage (CCS) in geological formation has become a promising option to achieve the goal of stabilization of atmospheric concentrations of greenhouse gases set at the United Nations Framework Convention on Climate Change. The key issue in global deployment of geological CCS technology is gaining the acceptance of regulators and the general public, a process that requires scientific risk assessment and cost estimation to understand the full implications of CCS. Predictive modeling of multiscale and multiphysics subsurface systems for CO_2 geological sequestration requires accurate data-driven characterization of the input uncertainties and understanding how they propagate across scales and alter the final solution.

In this project, we will leverage as much as possible existing state-of-the-art tools to provide uncertainty quantification (UQ) capabilities for the suite of simulation tools and integrate them together as a UQ pipeline. A quantification toolkit and workflow management software involve individual uncertainty quantification tools such as sampling methods, statistical analysis methods, numerical integration routines, response surface evaluation, and workflow management capabilities. The toolkit and software will provide a reliable means of quantitatively predicting the uncertainty of and assessing the risk to CO_2 geological sequestration, information that is of significant value to DOE and to our nation.

In FY 2011, we developed a prototype of the Middleware for Data-Intensive Computing Integration Framework (MeDICi)-based UQ and risk assessment workflow pipeline by coupling input uncertainty characterization, sampling generation, ensemble sampling simulation runs at supercomputer centers, analyzing ensemble results, and visualizing the statistical results together. These results were presented at an IEEE/ACM international conference. We developed a demon that can automatically generate ensembles based on given uncertainty distribution, conduct parallel ensemble runs at supercomputer centers, transfer simulation output files back, and visualize uncertainty associated with carbon sequestration to illustrate the capability of our MeDICi-based workflow for uncertainty quantification of carbon sequestration simulations. The developed workflow prototype laid a solid cornerstone for developing a UQ and risk assessment pipeline for carbon sequestration simulations for testing during the next fiscal year.

For a UQ study on the impact of uncertainty and heterogeneity of spatial permeability field on the CO_2 plume radius propagation, we employed both the quasi-Monte Carlo method and probabilistic collocation method to generate permeability sampling inputs for eSTOMP and conducted the ensemble runs using eSTOMP on large-scale supercomputer centers. Additionally, we developed an adaptive response surface method that can adaptively guide the sampling location and greatly reduce the computational cost in ensemble runs to study the relation between the uncertainty and heterogeneity of spatial permeability field on the CO_2 plume radius. We are currently drafting a peer-review journal manuscript to report our results. Further outcomes from this past fiscal year have included the creation of research quality codes for building adaptive response surface and for developing fast sampling method to reduce the computation cost for uncertainty quantification.

In FY 2012, we will continue to develop the UQ and risk assessment workflow pipeline for CSI and integrate more UQ components into the pipeline. We will develop efficient CSI UQ and model calibration methods and software tools and continue to publish peer-review papers in top journal publications.



MeDICi-based uncertainty quantification data and workflow management pipeline for carbon subsurface sequestration.

Understanding the Sources and Consequences of Uncertainties

Richard H. Moss, Jennie S. Rice, Michael J. Scott, Stephen D. Unwin

◆ This project is developing and demonstrating appropriate methods for uncertainty characterization (including uncertainty quantification and propagation) in the integrated Regional Earth System Model (iRESM) framework. Research results will inform iRESM model development and the design of numerical experiments. Addressing uncertainty rigorously is key to evaluating model results and providing useful information for climate change mitigation and adaptation decisions. ◆

The iRESM modeling framework aims to capture important feedbacks and interactions among three natural earth (climate, hydrology, and ecosystem) and two human (energy and socioeconomic) systems. These interactions occur within and between individual sub-national geographic regions in the context of national and global changes in these same systems. In addition, iRESM is intended to provide policy-relevant insights into the complex interactions between these five systems in a regional context and to help decision-makers understand the regional consequences of climate change as well as the consequences of policies to mitigate or adapt to such change within regions. To meet the twin requirements for scientific accuracy and policy relevance, the characterization of uncertainty must be accomplished in a computationally feasible, transparent, and practicable manner using a variety of methods.

In FY 2010, this project developed a 10-step uncertainty characterization (UC) process predicated on the need to perform UC in the context of a particular decision. The key insight of this process is that, without the framing provided by a decision, it is impossible to judge the importance of any particular uncertainty—all uncertainties are potentially important in a vacuum. In addition, without a decision context to focus the uncertainty analysis on key variables, the dimensionality of the UC problem quickly becomes intractable. The UC process for iRESM first identifies stakeholder decisions and decision criteria (i.e., metrics) and then systematically determines the relevant sources of uncertainty in each iRESM component model, testing the importance of those uncertainty sources for the decision criteria with sensitivity analysis. Next, only the uncertainties in these key sources are fully characterized (e.g., with probability distributions), and the process concludes with uncertainty propagation of these key uncertainties.

In FY 2011, project research focused on initiating a demonstration of the UC process developed in FY 2010 and analyzing the run time implications of uncertainty propagation for the iRESM framework. The results of these efforts are documented and summarized below.

Demonstration of the UC process. This project used the results of iRESM research into stakeholder decision support needs in the pilot region (U.S. Midwest) to provide a decision context for the demonstration. This research indicates that the human-environmental system interactions surrounding the penetration of renewable technologies are a key issue for the region. Depending on the specific stakeholder, many decision criteria may be pertinent, but for this demonstration, the project team chose to focus on regional electricity prices. Several iRESM component models are involved in the simulation of regional electricity prices: the regional climate model (RESM), the building energy demand model (BEND), the regional integrated assessment (energy-economy) model (R-GCAM), and the electricity infrastructure siting model (SITE). The project team met with each modeling group to determine the sources of uncertainty in each model that might affect the calculation of electricity prices. As described in the FY 2010 annual report, the following four sources of model uncertainty are present in the iRESM framework: input quantification, model skill, model completeness, and model implementation and integration. For this demonstration, the uncertainty source identification focused on input quantification and model skill/model completeness issues. The results are shown in the table below for each model and include the a priori judgment of each modeling team regarding the uncertainty sources likely to be most sensitive (i.e., important).

Run time analysis. Due to the large number of simulations required for a sufficient sample size, it is possible that run time issues may arise in propagating uncertainties across the coupled models of the framework. Initial work completed during FY 2011 suggests that run times may be extremely long (running to months on a parallel processing platform with ~2000 cores available) for fully integrated runs of the complete iRESM suite. The team will investigate flexible architectural approaches to shortening run times by running component codes on a coarser grid and/or using larger time steps. In addition, the team will investigate as necessary the use of fast-running surrogate models based on reduced-form processes or statistically derived response surfaces to emulate the behaviors of the detailed component models while having substantially shorter run times. In addition, the new computing resources available through a recent institutional computing investment (14,000+ cores available) may resolve some or all run time issues for uncertainty propagation.

In FY 2012, this project will have two primary tasks. First, the project will support the implementation of the uncertainty characterization methods in the numerical experiments demonstrating the iRESM prototype. The second task will investigate and develop specific methods to address the challenges of uncertainty propagation in iRESM. This task will research methods that have been used in the climate and Earth system, impacts assessment, and integrated assessment modeling communities, and develop recommended methods for iRESM applications that will take maximum advantage of new computing resources becoming available at PNNL.

Sources of Model Uncertainty Relevant to Electricity Prices in iRESM Component Models

Mode	Input Quantification	Model Skill/Model Completeness	*a priori* Judgment of Sensitive Uncertainty Sources
RESM	• Different physics parameterizations • Boundary conditions (from global climate model ensembles) • RESM initial conditions	• Different physics representations • Bias correction may not be appropriate for future climate • Possible issues with interactions between the physics and the scale of the model • Unknown unknowns	• Alternate physics more important than inter-annual variability over long run (the opposite in the short run) • Land surface processes • Cloud processes
BEND	• Count of building types in a region • Building stock characteristics • Necessary spatial resolution • Inputs from RESM and R-GCAM	• Representative-ness of locations chosen to represent the region • Count of buildings by building type is calibrated to reproduce base year total annual energy demand and hourly electricity profiles	• Uncertainty in climate likely to dominate uncertainties in base year building inventory • Demand response to price changes (interactions with R-GCAM) • Technological change (from R-GCAM)
R-GCAM	• Socioeconomics • Policy • Resource Base • Technologies • Climate (from RESM)	• Market clearing approach not consistent with electric system regulatory framework or water rights framework • Model assumes decisions are made rationally • Electricity system not modeled explicitly • Industrial sector not modeled at same detail as energy, transportation, agriculture	• Policy • Resource Base • Technology Characteristics • Climate
SITE	• Criteria used to mask unsuitable land including policy and social issues • Parameters LMP-based siting and grid interconnection cost algorithms • GIS layers are from different dates and resolutions • Technology siting requirements • Inputs from upstream models	• Technology siting order, mix affects results • Choice of objectives for siting algorithms to simulate regional planning • May overstate or understate restrictions on suitable land • Choice of spatial resolution—finer resolution better represents land-based constraints • Details of local policies not captured • Future policies, technology requirements are unknown unknowns	• Suitability criteria • Parameters and structure of siting algorithm • Future land and technology policy • Water availability

Energy Supply and Use

A Statistical State Prediction Methodology to Improve Reliability and Efficiency of Power System Operation

Ning Zhou, David J. Haglin, Francis K. Tuffner, Yousu Chen, Thomas A. Ferryman, Guang Lin, Jian Yin, Maria Vlachopoulou

◆ Motivated by the challenges of increasing uncertainty and variation brought in by the high penetration of renewable generation to power system operations, this project aims to develop a short-term prediction and uncertainty quantification methodology at grid level to enable well-informed proactive operations, which in turn improve power grid operation efficiency and reliability. ◆

A state estimator is an essential tool for power system operation. The estimated states reflect power system status and are the foundation of many essential operation decisions. Yet, due to the delays from communications and computations, current state estimators can only provide power grid status in the past. This delay has typically been in the range of 0.5–5 minutes. Operation decisions based on past states can lower the reliability and efficiency of power grid operation, especially when quick changes and large uncertainty are brought in by the high penetration of renewable generation.

The objective of this study is to enable operators to make well-informed proactive operation decisions by providing forecasted states. To achieve this goal, we plan to develop a short-term prediction and uncertainty quantification methodology at grid level from three perspectives: 1) the prediction method, which forecasts the values of power grid variables, 2) the prediction error (or uncertainty) quantification method, which gives the confidence interval of the forecast, and 3) the uncertainty propagation method, which calculates the prediction errors associated with the derived variables or states. It is expected that the study results will improve the situational awareness of an operator by providing a comprehensive look-ahead view of power system, which in turn allows time for proactive operations to improve power grid operation efficiency and reliability.

In FY 2011, our prediction efforts were focused on developing a prediction model and prediction methods for forecasting Net Interchange Schedule (NIS), which is defined as the sum of transactions (MW) between an ISO and its neighbors. Effective forecasting of NIS can improve the operation efficiency of an independent system operator (ISO). We obtained and parsed the data for forecasting the NIS from PJM, the largest ISO in the North America, to clarify the problem definition and performance metrics for NIS prediction. A server was set up for sharing and processing data. One prediction model was built with derived variables. Five forecasting methods (i.e., linear regression, stepwise regression, forward regression, supporting vector machine, recursive partitioning regression tree) are implemented, evaluated, and compared to predict NIS with lead time of 15, 60, 120, 180, and 240 min. The comparison shows improved prediction accuracy by about 20% over the scheduled NIS, which is used currently.

Methods	*Prediction in minutes*				
	15	*60*	*120*	*180*	*240*
Linear Reg.	6.64	6.80	6.75	6.81	6.76
Stepwise Reg.	6.61	6.81	6.73	6.75	6.77
Forward Reg.	6.56	6.62	6.65	6.70	6.74
SVM	22.26	23.85	23.48	25.01	24.22
Rpart	32.10	32.67	32.57	32.38	32.23
Scheduled	8.17	8.18	8.20	8.19	8.19

Measure of effectiveness for developed prediction methods over weeks 2-64.

Also in FY 2011, we set up an IEEE 30-bus system for studying uncertainty propagation method in the state estimation problem. For the non-linear models used in state estimation, there is no general analytical solution to propagate uncertainty. Therefore, Monte Carlo methods are usually used to circumvent the difficulty. Yet, because of huge size of a power grid, number of simulations needed by applying a classical Monte-Carlo is prohibitively large. To reduce the number of samples needed, based on sensitivity study, a smart sampling method was developed, implemented, and tested to propagate the uncertainty in the state estimation problem. The smart sampling method uses high-order uncertainty quantification algorithms on the sensitive variables and low-order uncertainty quantification algorithms on the insensitive variables to reduce the number of samples required to maintain acceptable estimation accuracy. It is shown through simulations that with 61 samples, the developed smart sampling method can achieve same estimation accuracy that requires 301 samples by a collocation method, which is already a sophisticate Monte Carlo sampling method.

The goal of FY 2012 work is to improve the performance of the prediction methods and building demo cases. Based on recent work, we plan to enhance the performance of prediction methods through developing an ensemble approach for prediction. A demonstration case will be built to show the prediction results using real world data. The sensitivity-based hierarchical smart sampling methods will be tested using mid-scale models and compared with other methods to improve performance.

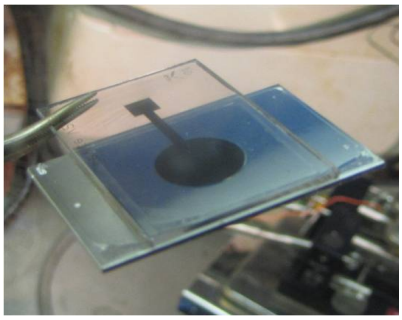
Alpha Voltaics

David E. Meier, Randall D. Scheele, Anne Kozelisky, J. David Robertson;
Jae W. Kwon, Jon M. Schwantes (University of Missouri)

◆ This project investigates the feasibility of converting the emissions from alpha emitting radionuclides into electrical power using a liquid-based semiconductor. ◆

Conversion technologies using radioactive decay as a power source were first conceived in the early 1900s and could provide orders of magnitude more energy density over current conventional chemical cell technologies of similar dimensions. Historically, "soft" beta emitters (emissions less than 300 keV) were used to mitigate efficiency loss due to radiation induced lattice defects within solid-state semiconducting matrices. Alpha particles have a devastating effect when allowed to attenuate through a solid-state semiconductor. The particles dislocate atoms and effectively create electron traps which eventually render the semiconducting power conversion device unusable.

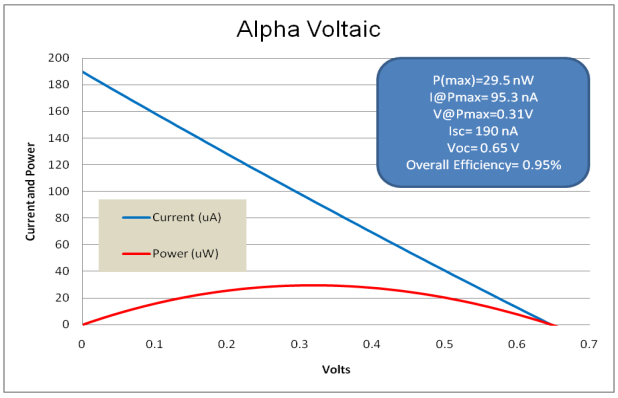
The goal of this project is to determine the feasibility of producing power by integrating an alpha emitting radionuclide into a liquid-based semiconducting conversion device. This project uses a liquid based semiconducting matrix as a way to mitigate the radiation induced lattice damage by promptly annealing any damage that is formed in the depletion region. Theoretically, this would permit the conversion of alpha particles (as well as other large ionizing particles) into usable electrical power over a long period of time.



Liquid semiconductor conversion device (inverted) loaded with Po-210.

The principle of the device is to convert the energy associated with each alpha decay into an electrical current. The device behaves similar to a Schottky diode with the semiconducting material (selenium and sulfur) acting as a depletion region that exists between two dissimilar metals. The devices are produced by our collaborators, Dr. Jae W. Kwon and his team at the University of Missouri, and have demonstrated successful power generation using a beta emitting isotope (^{35}S) as its source material. The University's role of this project is to provide devices that would be tested at PNNL.

Two radionuclides were used as source material for this project: ^{238}Pu and ^{210}Po. Plutonium-238 was identified as a practical radionuclide for this project due to its availability and a potential energy density of 0.49 mW/mg of PuO_2. Polonium-210 has a much shorter half-life (138 days), allowing for an even greater energy density of 85 mW/mg of $PoCl_4$. The radioactive compounds were directly incorporated into the liquid semiconducting materials and sealed inside the devices to be tested. Radiation field testing on devices was accomplished at the University of Missouri-Research Reactor, and surrogate tests showed that a high radiation field did not affect the device in any detectable manner.



IV curve of alpha voltaic loaded with Po-210.

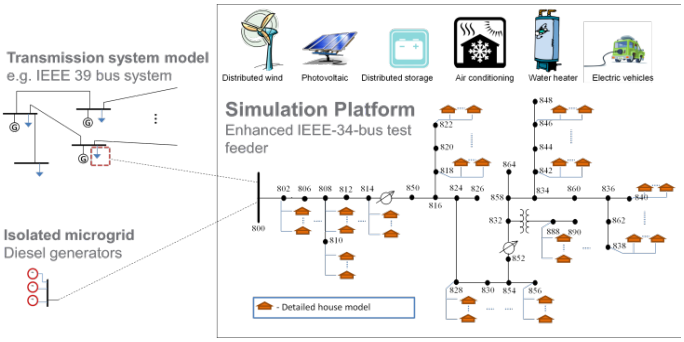
In FYs 2010 and 2011, we modified a glove box for use with our project. After thorough surrogate testing, an alpha-emitting radionuclide was loaded into a device and achieved minimal power production. The device tended to be short-lived due to polonium's affinity to metal surfaces. Plutonium oxide proved to be a difficult radioactive compound to use for this application as only minimal power was achieved, with the best result being ~ 3.1×10^{-4} % total efficiency. Chemical effects and self-attenuation of alpha particles due to particle size are potential reasons for lower than anticipated yield. Polonium-210 exhibited a significantly higher total efficiency, reaching nearly 0.67% and producing roughly 30 nW of power.

Follow-on work would include focusing on optimizing the device for use with the polonium isotope primarily looking at alternative materials in lieu of the metal surfaces of the device. Further, ^{210}Po can be produced in curie amounts using an indirect nuclear production method via the nuclear reaction $^{209}Bi(n,\gamma)^{210}Bi$ and its subsequent decay into polonium. The polonium can be separated from the bismuth using radiochemical techniques.

Centralized Control vs. Decentralized Control: Implications of Demand Response and Distributed Resources on Power System Security

Shuai Lu, Marcelo A. Elizondo, Nader A. Samaan, Ruisheng Diao, Karanjit Kalsi, Ebony T. Mayhorn, Yu Zhang, Chunlian Jin, Harold Kirkham

◆ The objective of this project was to investigate the potential impacts on power system reliability from applying centralized and decentralized control approaches on distributed energy resources (DER) and to provide guidelines to DER control design. The resulting simulation platform enabled the test of various DER control approaches in a distribution system, capturing voltage and frequency dynamics in either isolated microgrid mode or grid-connected mode. ◆



Simulation platform to test and provide guidance for DER control strategies.

Advancements in communications, information, and computer technologies have opened new opportunities to the control of generation, storage, and load resources in distribution systems. A well-designed DER implementation will maximize potential benefits that include improved reliability, higher operation efficiency, optimal use of renewable generation, and deferred infrastructure investment. In response to bulk power system changes, the control of DERs can be categorized into centralized control and decentralized control, depending on where the intelligent controller making the response decision is located. Centralized control sends the command signal from a central location (the utility or load aggregation company) to modify the load and adjust the output of the distributed resources. Decentralized control features autonomous response by each individual load or resource, monitoring signals containing system status information such as price, system frequency or voltage, or their derivatives. The performance and impacts of each specific DER controller design should be thoroughly evaluated before the actual implementation. Capability of modeling the steady-state and dynamic characteristics of the DER will help greatly in the design and operation of ongoing pilot programs and future large-scale implementations.

We studied the performance and effects on power system reliability from the application of centralized and decentralized control approaches for DERs using comprehensive dynamic modeling and simulations. The investigation identified challenges and provided initial guidance for design of DER controls. Important outcomes of the project include the study results on the characteristics in terms of predictability and response time, the impacts of each DER control approach, and as a testing platform and testing cases that can be used to evaluate different DER controller designs for both steady-state and dynamic performances. These outcomes provides valuable information and tools for the formation of smart grid DER control strategy and helps maximize the benefit of DERs for the power grid.

During FY 2010, we developed a simulation test platform with generic quasi-steady state and dynamic DER models such as rooftop photovoltaic, distributed wind generators, and detailed air-conditioning and water heater representations. The platform consists of a detailed distribution feeder connected to a transmission system model. Basic demand response control strategies were implemented and simulated. We investigated different interaction patterns among DERs and studied how traditional load shapes in distribution systems change with the inclusion of DERs.

In FY 2011, we improved the simulation platform. We improved the air-conditioning model; implemented a new, more realistic water heater model; and modeled an electric vehicle battery. The first research direction was optimal control and coordination of DERs. We identified this research direction after applying the simulation platform to an isolated microgrid, where DER benefits are more evident and their control coordination more challenging. In this part of the work, we coordinated centralized and decentralized control to maximize wind generation and improve frequency dynamics and identified the need for DER optimal control and coordination. The second research direction was characterization of demand response capabilities to provide services traditionally provided by generation with comparable quality of response in terms of predictability and timing. We analyzed the response capability of load controlled in open loop with a centralized signal and two types of decentralized control schemes (on/off response and droop response to frequency and voltage deviations).

Our findings emphasize the need for appropriately designed control strategies to maximize the benefits of DERs.

Decision Support for Future Power Grid Organizations

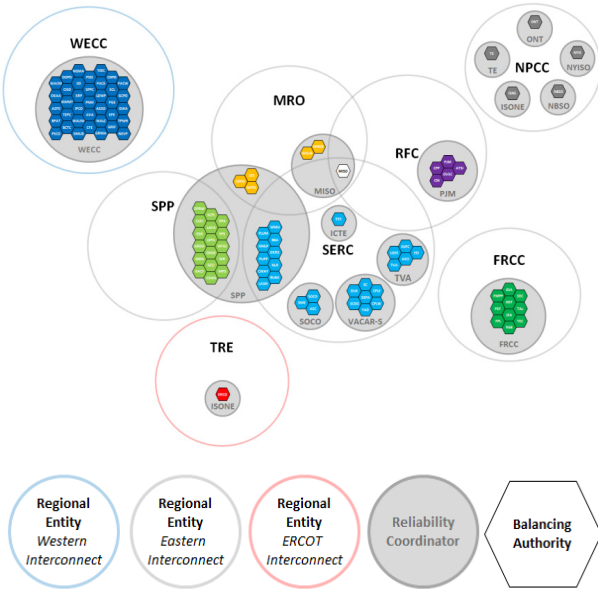
Gariann M. Gelston, Angela C. Dalton, Lucas C. Tate, Garill A. Coles

◆ We will systematically identify the human, contextual, and systemic factors present in the operation of grid operators' organization, investigate the underlying causes of past human error, and develop individual and organizational recommendations to improve the performance of the individual operators and thus the organization. ◆

Rapid and effective response to unknown, undefined, or unplanned system events is a core challenge for grid operators. This project analyzes the impact of better inter-organizational communication and coordination among grid entities on improving their distributed decision making under uncertainty, and develops a decision support system to enable rapid and adaptive decision making to ensure grid reliability. While previous research focused on improving individual operators' situation awareness and performance, we examine organizational communication and coordination to address the root causes of more complex, large-scale grid contingencies.

This research approach links across expertise in visual analysis, human factors, organization behavior, and emergency response to develop a systematic, organization-driven view of decision support. In addition, our studies will lead to an in-depth understanding of the key decisions, decision timescales, and challenges in organizational communication and coordination; help bridge the gap between grid reliability engineers and planners by enabling information sharing and better coordination; inform the design of innovative decision support technology; and develop decision support solutions to communication challenges for the current and future grid.

Our project goals include: 1) development of a role-based model to represent decision roles and inter-organizational relationships in the grid system, 2) identification of two target organization sets for model calibration, 3) engagement with the NERC and grid organizations in model development, 4) development of information framework for capturing decision goals, data sources, and industry tools, 5) sharing site visits summaries, research needs, and lessons learned with other projects, and 6) developing publications to describe modeling effort and decision support tool needs assessments.



North American regional partitioning.

During FY 2011, the project team developed a Bayes net model to represent critical organizational factors for grid operations to assess how inter-organizational communication and coordination affects system reliability. The project team made significant progress in building industry partnerships. Through NERC meetings and a presentation, the project team garnered support and willingness for further engagement from various grid entities. Important project findings so far include the following: 1) for unknown, undefined, and unplanned contingencies, automation cannot fully replace operators' decision making, 2) the type, nature, and frequency of communication for distributed decision making across the industry is highly variable and complex; a one-size-fits-all approach is unlikely to accurately represent this operational reality, and 3) both stochastic modeling and in-depth organizational studies are needed to enhance the empirical validity and generalizability of project outcomes.

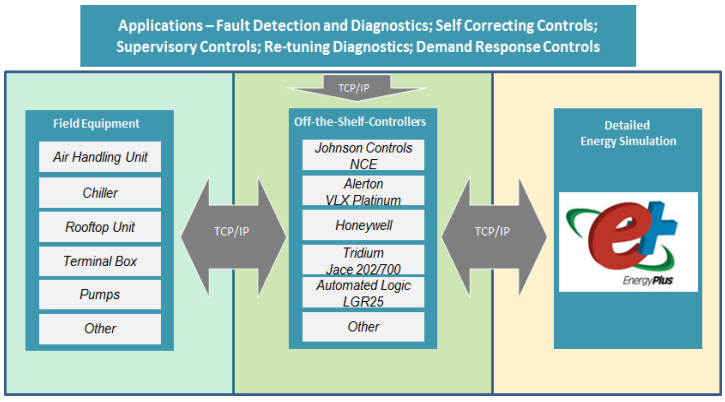
Based on the model developed in FY 2011 and the research compilation on grid complexity and organizational inter-dependencies, we are focused on research agenda for FY 2012. We will enhance the existing model to ensure an accurate representation of organizational decision structures and model calibration by leveraging existing PNNL expert elicitation technology with industry partners. We will extend efforts to system dynamic modeling to assess the impact of feedback and temporal variations. In addition, we will conduct case studies of grid organizations to understand the nature of interorganizational communication, as well as perform an economic impact analysis of operations and planning to develop recommendations that could lead to greater efficiency and effectiveness in short- and long-term decision making. The research outcome planned for FY 2012 will serve as a solid foundation on which interactive analytical approaches such as serious gaming might be developed for model validation, scenario analysis, and simulator-based training to engage industry with developed technologies.

Development of a Diagnostics and Controls Test Platform

Srinivas Katipamula, James K. Goddard, Michael R. Brambley, Hung Ngo

◆ This project will develop a framework to test automated fault detection and diagnostics and advanced and self-correcting controls algorithms and tools in a laboratory environment. ◆

As buildings use over 40% of total energy and over 70% of electricity in the United States, they have a significant impact on national energy use and the environment. With this significant usage, 10% to 30% of energy in U.S. commercial buildings is wasted from improper operations. Solutions to reduce fossil fuels and carbon emissions require significant contributions from the buildings sector. Part of the reason many buildings fail to perform as well as expected is degraded equipment, failed sensors, improper installation, poor maintenance, and improperly implemented controls. Automated fault detection and diagnostics (AFDD) and advanced and self-correcting controls can help eliminate this energy waste. However, an obstacle to developing AFDD tools and controls in buildings is the absence of a laboratory to develop and test diagnostic tools and control algorithms in real and simulated environments.



Various building controllers are used to test and validate AFDD and advanced control algorithms. A detailed energy simulation program (EnergyPlus) is integrated to simulate building thermal loads, while controllers emulate building controls in a field-like environment. All communication between various components in the framework use TCP/IP communication protocols.

This project will create and extend the limited laboratory capabilities to design, development, and testing of both AFDD and advanced control algorithms. AFDD is a programmed process by which faulty operation, degraded performance, and broken components in a physical system are detected and understood. AFDD tools are based on algorithms that process data to determine whether the source of the data is experiencing a fault. Ongoing, non-automated maintenance of building systems as usually performed is notably ineffective and may be suboptimal, being almost exclusively complaint-driven and "quick fix" oriented. The enhanced laboratory will be capable of testing advanced smart grid demand response algorithms targeted at large commercial buildings. Development of this capability will enhance our national leadership in this field.

As part of this effort, we created a controls and diagnostics laboratory that allows us to design, develop, test, and validate AFDD as well as advanced controls algorithms in a laboratory environment. A number of off-the-shelf building controllers from a number of vendors (Johnson Controls, Honeywell, Automated Logic) were networked for testing and validating algorithms. The controllers can be configured to govern a number of building systems, such as air handling units, zone variable air volume boxes, chillers, and boilers. The building controllers were also configured to control the air handling unit remotely in the heating, ventilation, and air conditioning laboratory. This remote control capability allowed us to test and validate control and diagnostic algorithms in a field-like environment.

Because the heating, ventilation and air conditioning laboratory currently only has an air handling unit, many other systems cannot be directly tested. Instead, we developed a physical framework to simulate building and systems using a detailed simulation model, EnergyPlus. This simulation/emulation framework used an open source Building Virtual Control Testbed to integrate EnergyPlus and the off-the-self controllers. The framework provided a simulation of buildings and their systems while controls were emulated using real controllers. The virtual control test bed allowed for the integration of the simulation and the emulation processes, including testing supervisory controls, diagnostics algorithms, automatic reconfiguration of controls (when faults are detected), and condition-based maintenance algorithms. In addition to testing AFDD and advanced controls, the framework tested concepts relevant to the integration of buildings with electric power grid. For example, the framework simulated price-based controls in a prototypical office building, where the price of electricity changed hourly and building controls reacted to price signals.

The capabilities developed as part of this effort provide a framework to test AFDD algorithms, fault-tolerant controls, and advanced controls in field-like environment. These algorithms and advanced control concepts will allows us make the commercial building stock more efficient and enable the buildings to integrate seamlessly with the Smart Grid.

Development of a Regional Energy and Infrastructure Systems Framework

Michael C.W. Kintner-Meyer, Jennie S. Rice, Timothy E. Seiple, James A. Dirks, Will J. Gorrissen, Olga V. Livingston, Brandon J. Carpenter, Chunlian Jin, Erin L. Hamilton, Nino Zuljevic

◆ This project is developing a Regional Energy Infrastructure Framework (REIF) consisting of tools and models to analyze the impacts of climate change and the associated mitigation and adaptation strategies on the energy infrastructure. ◆

The integrated Regional Earth System Model (iRESM) is developing and testing new systems modeling frameworks and tools that integrate climate with hydrology, land systems, socio-economics, and energy at the regional scale to enable regional feedbacks and interactions between energy, hydrology, climate, biogeochemistry, and global implications of socioeconomic processes to be evaluated. This analytical framework will address a knowledge gap for regional infrastructure planners to design energy infrastructure that will be resilient, affordable, and flexible to sustain new conditions imposed or caused by climate change.

Current toolsets do not provide an efficient and integrated way to address the technical and economic complexities of siting, expanding, and operating new infrastructure at a sufficient level of detail for investment decisions in the context of climate change and climate policy uncertainties. This project initiates a development process to fill this methodological gap.

Throughout the course of this project, the following set of models will be developed:

- A power plant siting model (called SITE) that considers locational marginal prices for energy, land-use availability, and spatial considerations such as exclusion zones and distances to necessary infrastructures for fuel or the transmission grid. This model will utilize highly resolved geospatial data sets of land-use, water resource availability, renewable energy resources, and transportation infrastructures as well as energy infrastructure for fuel input and energy service delivery.
- A model for electricity demand (MELD) representing the building stock, electric vehicle transportation, the manufacturing sectors, and their response to population and economic growth and weather dependency, and advanced demand response strategies enabled by smart grid technologies. This model will calculate the electricity demands hourly for 1 year.
- An electricity operations model (EOM) that simulates the operation of the electric grid. It considers the economics of individual power plants and the characteristics of the transmission system to perform an economic dispatch of power plants to meet hourly loads. The model will be linked to iRESM's hydrological model to assess whether or not sufficient water resources are available for normal operation of power systems. The model will be responsive to weather induced loads, such that severe weather conditions and their full impact on the infrastructure can be analyzed.

Among our accomplishments in FY 2010, we developed geographic information databases that would store relevant geographic data sets in a format that can be easily accessed, analyzed, and used for visualization purposes. We also developed analytics tools to perform complex, nested queries on geographic datasets. We tested feature extraction methods to characterize buildings stock for buildings electric load modeling. Finally, we developed a building model and made significant progress in disaggregating system load profiles to attribute the contribution of the commercial and residential building sectors to the entire system load.

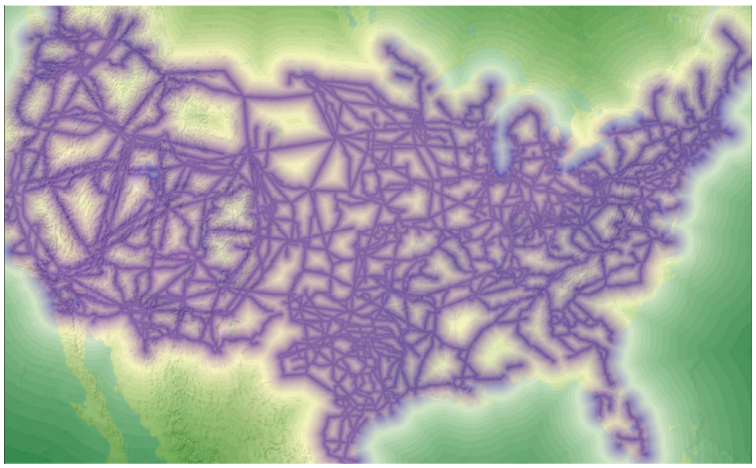
During FY 2011, our project accomplished the following with each model.

SITE model. We oversaw migration from a desktop to a multi-core high internal memory machine for large-scale geographic information system (GIS) analyses. All data and software were migrated to the new machine. The new machine achieved a speed up of at least 50 times without optimizing any code. In some cases, we are able to perform analyses not previously possible in a workstation environment. For example, calculating distance to energy assets for the entire country at 30-m resolution requires several hundred GB of RAM to complete.

Consolidating iRESM relevant GIS data into one consistent format allows queries across 137 data layers of energy infrastructure, natural resources, land-use, population, and other data with a 1 × 1 km and 30 × 30 m resolution. This GIS database supports the energy infrastructure, water management, and land-use modeling activities. All data can be made public to share with research community. Additionally, we developed open-source GIS analysis tools to perform large-scale queries to identify suitability of land given a set of complex criteria. The novelty of the GIS analysis tools is that it is open-source, scales well with spatial resolution of data, and has no limits/constraints on the number of criteria for site evaluations and selections. Further, it computes distances functions from any location to existing energy infrastructure and natural resources, such as body of

water or rivers. Finally, we completed the first version of SITE that utilizes the GIS queries in a defined form to evaluate the ability to site new electricity generation capacity within a given utility region and to determine the grid-interconnection cost.

MELD model. We completed a design document describing the functional blocks of the model, data requirements, and interactions. Significant progress was made on the Building Energy Demand Model (BEND), where we now have the capability to model thousands of unique buildings within a particular geographic region and proportionally weight the output such that a regional electric demand profile can be generated. We completed a white paper on transportation and industrial and service demand that describes how these demands will be modeled and how they can be expected to change with changes in locational marginal prices developed by the EOM.



iRESM relevant GIS data showing queries across multiple data layers of energy infrastructure, natural resources, land use, population, and other data.

EOM model. We performed a review for an open-source electricity operations model to be used within iRESM. The outcome of this review indicated that PNNL's Renewable Integration Model (RIM) will provide the fastest and lowest cost approach toward providing an electricity model. Further, we developed a tool to adjust the electric load inputs into our current electricity operations model (PROMOD). We analyzed the impacts of severe weather in the summer time on the grid in the Great Lakes region to test the sensitivity of the electric grid to severe weather conditions. The preliminary results are suggestive of a high sensitivity of the electric grid with respect to hot and humid conditions over longer periods of time.

During FY 2012, we will work toward accomplishing the following tasks:

- Expand the suitability criteria and siting analyses beyond a generic thermal to address specific thermal technologies
- Implement and test coupling/interactions with other iRESM models
- Implement and test interactions with EOM
- Expand electric infrastructure modeling to address additional energy infrastructure components
- Finalize the integration module
- Refine the functional specifications for EOM modifications for use in iRESM
- Complete our development of the prototype EOM

Integrate EOM with SITE and BEND/MELD, and complete testing.

Development of Rechargeable Li/air Batteries

Jason Zhang, Wu Xu, Jie Xiao, Vilayanur V. Viswanathan, Jianzhi Hu, Silas A. Towne

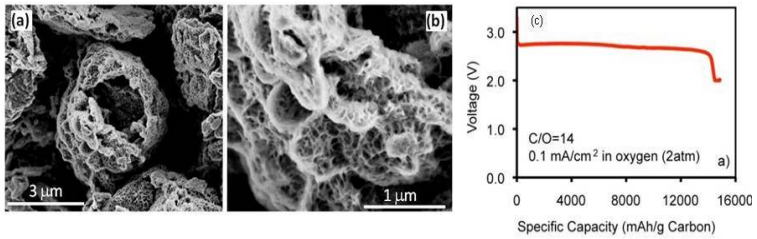
◆ Energy storage devices, especially batteries with good reliability, affordability, and environmental friendliness for plug-in hybrid electrical vehicles (PHEVs) and pure electrical vehicles (EVs), are critical for the United States. While the current lithium (Li) ion battery technology can satisfy the short-term need of EVs, rechargeable Li-air batteries are one of the most promising energy storage technologies for the next generation of EV applications. ◆

Li-air batteries have a much higher specific energy than most available primary and rechargeable batteries. They exhibit a theoretical specific energy of 2,790 Wh/kg, which is more than five times higher than conventional batteries. Although several authors have reported the significant rechargeability of Li-air batteries, there are still many questions and uncertainties on the stability of these batteries. The main goal of this project is to investigate the rechargeability of these rechargeable Li-air batteries and understand their fundamental mechanism.

In FY 2010, we designed a system that can be filled with O_2 so that Li-O_2 battery rechargeability can be tested in situ or ex situ in a controlled environment. The cycleability of lithium peroxide (Li_2O_2) in air electrodes with Super P (SP) conductive carbon with or without catalysts was also tested. Gases released during charge were measured by GC-MS analysis with Li_2O_2 showing decomposition in the given electrolyte under 4.5 V. However, we also found that the carbonate-based electrolytes are unstable during Li-air battery discharge.

During FY 2011, the Li-O_2 chemistry in nonaqueous liquid carbonate electrolytes and the underlying reason for its limited reversibility was systematically investigated. The discharge products collected from the air cathode in a Li-O_2 battery were analyzed using x-ray diffraction. Lithium alkylcarbonates and lithium carbonate (Li_2CO_3) are the main products. On the other hand, neither lithium peroxide (Li_2O_2) nor lithium oxide (Li_2O) was detected. More significantly, in situ gas chromatography/mass spectroscopy analysis revealed that Li_2CO_3 and Li_2O cannot be oxidized, while LPDC, LEDC, and Li_2O_2 are readily oxidized, with CO_2 and CO released. O_2 was evolved from the oxidation of Li_2O_2. The apparent reversibility of Li-O_2 chemistry in an organic carbonate-based electrolyte is actually an unsustainable process that consists of the formation of Li alkylcarbonates through the reductive decomposition of carbonate solvents during discharging and the subsequent oxidation of these same alkylcarbonates during charging. Therefore, a stable electrolyte that does not lead to an irreversible byproduct formation during discharging and charging is necessary for Li-O_2 batteries that are truly rechargeable.

High capacity air electrode was developed in FY 2011. We demonstrated that with appropriate manipulation, functional graphene sheets can self-assemble into hierarchical porous architectures with highly interconnected pore channels. The porous graphene exhibits different physical and chemical characteristics compared with the reported properties of previous graphene sheets. The novel air electrode consisting of the porous graphene delivers a capacity in Li-air batteries of 15,000 mAh/g, the highest reported value in the Li-air field. This excellent performance is attributed to the unique bimodal porous electrode structure, which consists of microporous channels facilitating rapid O_2 diffusion, while highly connected nanoscale pores provide a high density of reactive sites for Li-O_2 reactions. We show that defects and functional groups on graphene favor forming isolated nano-sized Li_2O_2 particles to prevent air blocking in air electrode. The hierarchically ordered porous structure in bulk graphene enables its practical applications by promoting accessibility to most graphene sheets in this structure. Our research has led to 10 publications on Li-air batteries, most notably a chapter in the *Handbook of Battery Materials* (Wiley-VCH Publishers 2011) and an article in the *Journal of Power Sources*.



(a) and (b) SEM morphologies of the graphene-based air electrode, which show both microporous channels facilitating rapid O_2 diffusion while the highly connected nanoscale pores provide a high density of reactive sites for Li-O_2 reactions, (c) The air electrode demonstrated a record capacity of 15,000 mAh/g.

In FY 2012, our efforts will focus on the development of new electrolytes and air electrodes which are stable in both charged and discharged state. Novel catalysts for O_2 reduction and evolution will be developed to improve the battery performance and to reduce the over-voltage during the charge process of the Li-O_2 batteries. The success of this project will enable a practical application of a novel Li-O_2 battery system and significantly improve the energy density of Li-O_2 batteries for EV applications.

Development of Regional Agriculture-Land Use Models

Allison M. Thomson, Roberto C. Izaurralde, Tristram O. West, Marshall A. Wise, Benjamin Bond-Lamberty, Katherine V. Calvin

◆ We are developing an advanced capability for simulating climate impacts on agriculture and forestry to allow investigation of adaptation needs and mitigation potential of land management. This will inform questions about food security and greenhouse gas mitigation from regional-scale agriculture of interest to decision-makers. ◆

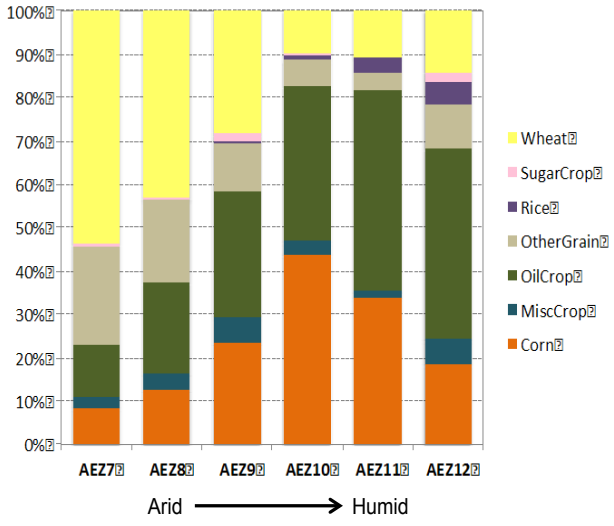
Climate change and food security are global issues that are increasingly linked through decision-making that takes place across all scales from on-farm management to international climate negotiations. While still supplying sufficient food to feed the global population, understanding how agricultural systems can respond to climate change through mitigation or adaptation thus requires a multi-sector tool in a global economic framework. Integrated assessment models are one such tool; however, they are typically driven by historical aggregate statistics of production in combination with assumptions of future trends in agricultural productivity; they are not capable of exploring agricultural management practices as adaptation or mitigation strategies. Yet, there are agricultural models capable of detailed biophysical modeling of farm management and climate impacts on crop yield, soil erosion, and carbon and greenhouse gas emissions, although these are applied at point scales incompatible with coarse resolution integrated assessment modeling.

To combine the relative strengths of these modeling systems, we are applying the agricultural model Environmental Policy Integrated Climate (EPIC) in a geographic data framework for regional analyses to provide input to a regional integrated assessment model (Regional Global Change Assessment Model [RGCAM]). The initial phase of our approach focuses on a pilot region of the Midwestern United States. We have developed the necessary data and modeling capability to apply EPIC across the domain at 56 m spatial resolution and use the results, in combination with detailed USDA data and remote sensing products, to inform GCAM. This will enable integrated assessment to take into account the different crop yield, bioenergy production, soil carbon, greenhouse gas emissions, and economic costs of different management practices for agriculture. Using this information, GCAM can simulate the optimum mix of land management to achieve specific climate mitigation or adaptation targets.

In FY 2011, model development advances led to detailed integration planning and testing. The agriculture and land use components of the integrated assessment model have been tested with the new subregional capability and with multiple crop production, including important crop rotation, methodologies in the simulations. This global data framework can now be used as boundary conditions, and we have developed a new data template for the pilot region of interest. We have identified what in the data template will be provided by the EPIC model and begun simulations. The EPIC model has now been extensively tested on supercomputing platforms and is ready for application using the spatially explicit modeling framework already completed. The new integrated assessment model code structure has been further tested for crop rotations and an expanded selection of bioenergy crops.

In the next fiscal year, this project will use a combination of data and EPIC model results to re-calibrate the GCAM initial year agricultural system for our pilot region to include multiple management options for climate mitigation. We will further this capability by incorporating climate change impacts from a PNNL regional climate model into the EPIC simulations and run the crop model iteratively with the GCAM model to dynamically simulate the agricultural mitigation response to changes in climate. These pilot region tests will enable us to expand the new capability to larger areas and to different regions of the world.

The outcome of this project will be an integrative element of the final integrated Regional Earth System Model and will connect physical science and human elements of the model framework through land productivity and management.



Results illustrate how defining subregions based on climate characteristics provides detail on what crops may be grown in different regions in the future, with arid regions growing a greater proportion of wheat and humid regions a greater proportion of corn and soybean.

Enhanced Light Extraction by Mesoporous Layer of Graded Refractive Index for Highly Efficient Organic Light-Emitting Devices

Liang (Frank) Wang, James S. Swensen, Birgit Schwenzer, Daniel J. Gaspar

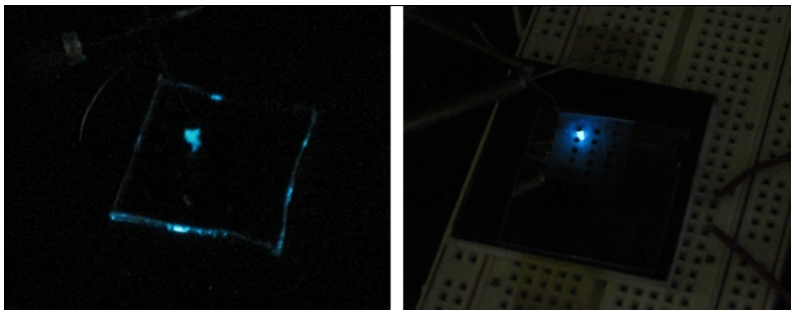
◆ This project is aimed at developing a technology that enables energy efficient white organic light emitting device (OLEDs) for solid-state lighting through the development of a graded refractive index structure to include in an OLED that increases the amount of light emitted, thereby improving overall device efficiency. ◆

OLEDs have the potential to reduce the amount of electricity used for lighting significantly, which represents 18% of total electricity usage plus another 4-5% to remove the heat generated by inefficient lighting. OLEDs consist of layers of organic light emitting materials sandwiched between two electrodes. The goal for OLED technology is to reduce cost, improve lifetime, and increase efficiency. The external quantum efficiency (EQE) represents the efficiency with which electricity is converted into light and efficiency of extracting emitted light out of the device. Currently, the EQE of OLEDs is limited to approximately 25% due to light trapping inside the layers of the device.

A number of approaches have been pursued to improve the EQE and amount of light emitted from OLEDs. The primary loss mechanisms are due to light trapped in the organic layers, caught in the glass substrate, and lost due to quenching by the reflective electrode. Light extraction methods have been proposed to target losses to the first two trapping modes; effective approaches were demonstrated for reducing total internal reflection and improving light extraction at the glass-air interface (microlenses, photonic crystals, dielectric mirrors, and very-low-index aerogels). This project will increase the amount of light extracted from the organic layers, the first and most important source of losses. In contrast to a common method to improve the amount of light extracted from the organic layers – the use of wavelength-scale periodic gratings applied between the glass substrate and transparent electrode – our approach is applicable to white OLEDs for general purpose lighting.

A light extraction technology that functions broadly over the visible spectrum at low processing cost is needed. Our approach to the total internal reflection is to reduce the index of refraction mismatch, thereby reducing the critical angle, leading to more light escaping from a given layer. This method of improving external quantum efficiency by refractive index matching has the advantage of use in white OLEDs across the visible wavelength range. Our approach utilizes solution processing methods to generate a robust inorganic film with an index of refraction, η, that can be tuned across the entire range of organic (η~1.8) and glass (η~1.4) layers. We examined a range of processing conditions and a range of additives to generate films with the appropriate optical and physical properties: tunable index of refraction, smooth surface, and compatibility with downstream processing steps.

A number of films were characterized by atomic force microscopy, x-ray diffraction, nitrogen adsorption, ellipsometery, UV/Vis spectrometry and other techniques to understand the interplay between film processing, optical properties and physical properties. The films exhibited an acceptable surface roughness and compatibility with deposition of transparent conducting oxide electrodes deposited using multiple methods. We were able to demonstrate the ability to stack at least two layers with a range of η, such that a fairly continuous transition is obtained from the η~1.8 to η~1.4.



Operating OLED without (left) and with (right) the light extraction layers. By including the light outcoupling layers, we are able to couple more light into the glass substrate and reduce waveguiding in the glass substrate.

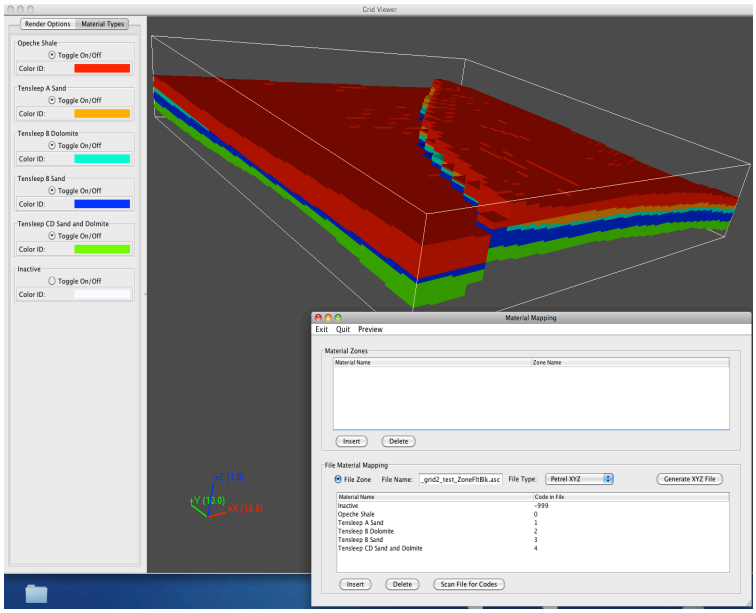
Most importantly, our films significantly reduce the light trapped in the organic layers of the device. Although initial measurements using OLED test structures highlight the difficulty of accurately quantifying the enhancement factor of these structures using very small OLED devices, we were able to measure the optical emission as a function of angle. This clearly demonstrates that our light extraction films generate emission into a much larger solid angle, confirmed by micrographs showing no discernable light emitting from the edge of OLEDs with our light extraction film (indicating all visible light at the optical microscopes intensity scale is redirected into the normal direction). OLEDs without our structure show significant edge emission from total internal reflection. In FY12, we will optimize the coating process to reduce roughness, and incorporate films into larger OLEDs to quantify effectiveness in enhancing the external quantum OLED efficiency, and combining our films with OLEDs incorporating light extraction structures at the glass-air interface to maximize total light emission.

Geological Sequestration Software Suite: Numerical Model Development

Mark D. Williams, Signe K. Wurstner, Paul D. Thorne, Andrew P. Kuprat, Vicky L. Freedman, Vidhya Gurumoorthi, Duane L. Ward

◆ This Geological Sequestration Software Suite (GS^3) project will develop an integrated software system with a consistent user interface and data structures to provide for comprehensive, rapid development of simulations for greenhouse gas sequestration at specific sites. The ability to develop and run multiscale simulations with multiple conceptual models and operational complexity in high performance computing will facilitate evaluation of the efficacy of the sequestration approach, given the uncertainties of the natural environment. ◆

Fossil fuels will remain the mainstay of energy production well into the 21st century. The ability and availability of these fuels to provide clean, affordable energy is essential for the prosperity and security of the United States. However, increased concentrations of CO_2 from carbon emissions are expected unless energy systems reduce the carbon emissions to the atmosphere. One way of accomplishing this is through carbon sequestration: storing CO_2 in geologic formations, including oil and gas reservoirs, unmineable coal seams, and deep saline reservoirs. The goal of DOE's sequestration research is to understand the behavior of CO_2 when stored in geologic formations. This information is key to making sure that sequestration will not impair the geologic integrity of an underground formation and that CO_2 storage is secure and environmentally acceptable.



Material property assignment form for specifying hydrostratigraphy using a solid earth model option, along with a preview of the grid showing the resultant material distribution.

The focus of this project is to develop algorithms and tools for building multiscale numerical models from site conceptual models. This application will aid in translating conceptual models to a numerical modeling framework and provide the capability to generate multiscale (spatial and temporal) numerical models that support a variety of collaborative geologic sequestration studies. User specifications for numerical models include grids, geology, boundary and initial conditions, source terms, material properties, geochemical reactions, and geomechanics. To preserve the distinction between the conceptual model and its translation to a numerical modeling framework, the application manages data associated with each specification independently. This will facilitate: 1) building multiscale numerical models from a common conceptual model, 2) building numerical models from multiple conceptual models, 3) ease in regenerating numerical models in response to revisions of the conceptual model, and 4) revising the numerical model specification during the development process (e.g., grid modifications and resulting reassignment of material property values and distributions).

During FY 2010, a design concept was developed and presented to the project team and a prototype numerical model development tool with limited functionality was developed focused on supporting the CO_2 injection based operational mode of the STOMP-CO_2 simulator. The Java programming language was selected because the code is platform independent (Linux, Windows, OSX) and programs can be launched via Java webstart from the GS^3 wiki. The team adopted the Netbeans Integrated Development Environment for Java as a development platform because it provides for rapid graphical user interface form prototyping, design, and development. The XML format was selected for storing the model definition with JAXB parsers for reading and writing the files based on a pre-defined XML schema. Also, the XML format is widely supported, and the JAXB parsers are automatically generated within the Netbeans IDE. Portions of the model domain can be selected and properties specified based on simple indexing, geometric objects, and linkage to external files for more complex specification. For supporting complex hydrostratigraphy based on solid earth models (e.g., Earth Vision or Petrel), a work flow was developed for exporting the numerical grid, assigning properties to the grid within Petrel or EarthVision, and then importing the zonation back into the model definition process.

Progress during FY11 included completing the initial forms and user interface, XML schema/file structure, and

code for generating STOMP simulator input files for CO_2 simulations with IJK-type zone specifications. These capabilities enabled creation and generation of the two STOMP short course CO_2 test problems and a Mt. Simon Injection case with a radially-symmetric grid. Other major accomplishments included linkage to an OpenGL visualization toolkit (replacing the Java3D library implemented last year) for viewing grids, model hydrostratigraphy, and selected nodes/elements; linkage to the updated GS^3 Alfresco Content Management System for storing numerical model definition XML files and generated STOMP input files; added functionality for Solid Earth Models (e.g., EarthVision and Petrel) for mapping material codes in files to simulation material properties; selection logic for portions of the finite difference grid using polygons and lines; and tracking changes made to the model definition XML file based on user-supplied input.

A software demonstration was developed in August 2011 that integrated the entire prototype GS^3 system, including the features developed in this numerical model building project. Related to this project, the demonstration showed the process of creating/revising a numerical model definition and building STOMP simulator input files from which simulations were launched on remote workstations. This process involved in revising a numerical model definition XML file stored on the GS^3 platform included launching the Java numerical model development software from the GS^3 wiki using Java webstart, checking out the model definition XML file from the platform CMS, making revisions to the model definition locally on the client machine through the GUI, and then checking the revised XML file back into the CMS. Building a STOMP simulator input file from the model definition XML file is initiated throughout the GUI on the client machine and the resulting file is checked into the GS^3 CMS. A STOMP simulation using this input file can then be launched on a remote workstation with the simulation results, along with graphical output, stored back on the GS^3 CMS. The remote job launching functionality is part of the GS^3 platform-developed software.

Work during FY 2012 will focus on platform linkages for selecting external files from the GS^3 CMS used in the numerical model definition process, generating STOMP-CO_2 input files for simulations defined with external files, and supporting additional STOMP-CO_2 process models and features (both in the UI and input file generation). The additional STOMP-CO_2 features that will be supported include definition of chemical reaction networks important in geologic sequestration in saline reservoirs and new features currently being added to the simulator code (e.g., coupled well model and geomechanics).

High-Capacity Reversible Metal Hydride Air Battery

Ewa C.E. Rönnebro, John P. Lemmon, Birgit Schwenzer, Jun Cui

◆ Envisioning a sustainable technology, this project aims to provide a new high-impact approach to low-cost, large-scale stationary energy storage with efficient performance for the future renewable energy storage market. ◆

With the increasing demands on renewable energy, there is a need to store energy more efficiently in large-scale applications to supply the power grid. For grid-scale applications, the performance of existing high-capacity energy storage is a limiting factor. The commercial nickel metal hydride battery has a metal hydride anode and a nickel oxide cathode. This heavy metal oxide cathode severely limits the energy capacity and effectively lowers efficiency. One proposal is the advancement of a metal hydride air battery, a higher capacity, robust, long-life technology. The metal hydride air battery breakthrough technology would have a significant impact on meeting energy storage performance and cost targets for grid-scale storage applications. The key to realize this technology is to develop high-capacity metal hydride anode materials that enable high rates of mass transfer during cycling.

We are developing a reversible, long-life, high-capacity metal hydride air battery that can be manufactured using low-cost materials and processes. Our approach will combine novel, high capacity metal hydride anode materials with an efficient bi-functional air cathode while incorporating an aqueous alkaline electrolyte with common separator materials that will greatly reduce the cost of large-scale energy storage. We will replace the capacity-limited nickel hydroxide cathode with a lightweight bi-functional air cathode. By combining novel metal hydride anode materials with an efficient bi-functional air cathode with an aqueous alkaline electrolyte with common separator materials, the cost of large-scale energy storage will be reduced.

This metal hydride air battery technology will be made possible by developing high capacity metal hydride anode materials with protective coatings that enable high rates of mass transfer during cycling and serve as a barrier to oxidation from the aqueous electrolyte. Because the cathode in a metal hydride air battery does not limit capacity, we are using high-capacity metal hydrides. To accomplish a battery with superior capacity, we will need to focus on developing anode materials and to screen through candidates efficiently. The goal is to deliver a bench-top multi-cell stack battery capable of a 50-100Whr range at 50-100W power with superior capacity and cycle life relative to the state-of-the-art.

During FY 2011, the main accomplishments were 1) designing and fabricating a screening capability to identify promising, high-performing metal hydride candidates, 2) showing proof-of-concept of a small-scale prototype of the metal hydride air battery, and 3) down-select advanced anode materials concepts. First, we designed and manufactured an anode screening capability made up of nine electrochemical test cells to screen for the high-capacity metal hydride materials effectively. These test cells are based on a metal hydride anode and nickel hydroxide cathode similar to a nickel metal hydride battery. The baseline was established using the classical nickel metal hydride battery alloy $LaNi_5$, which has a capacity of about 200mAh/g. Promising, high-capacity materials can be screened through with respect to their performance (i.e., capacity and cycle life) and then selected for further testing in the metal hydride air battery prototype to achieve higher capacity. The challenge is that the high-capacity metal hydride material corrodes in the electrolytes. We have evaluated several innovative approaches and found a path forward to obtain advanced materials. The focus in FY 2012 will be anode materials development and demonstrating superior performance of an advanced high-capacity metal hydride material by using our solution to corrosion resistance.

We also assembled a small-scale metal hydride air battery prototype for initial operation with an anode baseline material, $LaNi_5$, with capacity of approximately 300mAh/g (300Wh/kg). The cathode is a light-weight carbon based material and the prototype has a thin nickel wire for charging anode. The next step is to replace the baseline material with low-cost, high-capacity candidates. The candidates, nine at a time, will be explored in the anode screening capability and the best candidates will be selected for further testing in the air battery prototype to obtain higher capacities. The goal in FY 2012 is to demonstrate a long cycle life and capacity of greater than 400mAh/g (400Wh/kg) of the metal hydride air battery which is an important step on the path to in the future be able to demonstrate 800Wh/kg based on advanced metal hydride materials, which would be superior to state-of-the-art of any other energy storage.

By the end of the project, we expect to have improved the performance and energy density of the anode by developing candidate high-capacity hydride materials with protective coatings in appropriate electrolytes. The efficiency of the air cathode will be improved by developing catalysts for the carbon-based material.

Integrated Emissions

Michael L. Elliott, Charles J. Freeman, Gary B. Josephson, Ward E. TeGrotenhuis, Daryl R. Brown, Sarah H. Widder, R. Scott Butner, Feng Zheng, Greg A. Whyatt, Robert S. Wegeng, Eddie G. Baker, George G. Muntean, David L. Brenchley, Mark D. Bearden

◆ This project combined PNNL's strengths in fundamental sciences and applied engineering to discover, develop, downselect, and optimize new processes for CO_2 and contaminant removal from the flue gas of coal-fired power plants. Several breakout technologies were identified and developed, and an R&D plan was established to support advancement of priority transformational solutions. ◆

Integrated emissions management is a methodology for reducing the cost of CO_2 and contaminant removal from the flue gas of coal-fired power plants. Conventional fossil fuel power plants remove only trace contaminants from their flue gas. In a carbon-constrained world, most or all of the CO_2 will have to be removed from flue gases. This will be prohibitively expensive using conventional means. The concept of integrated emissions management offers the potential of significantly reducing the cost of carbon capture and storage (CCS) from fossil fuel power plants. Integrated emissions management considers a single, integrated system to capture both carbon (CO_2) and criteria pollutants (NO_x, SO_x, Hg) using a whole-plant solution rather than as incremental emissions control units. This offers the advantage of utilizing new capture materials while using the existing plant infrastructure to reduce capital expenses.

DOE has set aggressive cost targets for implementing CCS into existing post-combustion coal plants as well as for new facilities. These targets cannot be met using current commercial offerings that are mostly incremental improvements to existing technologies, nor can they be met using conventional engineering retrofit philosophies. To meet the cost targets, significant reductions (factors of 2 to 10) must be made to both the capital costs and operating costs of current commercial offerings. This requires new capture materials and also leveraging equipment and energies that already exist in facilities. This project will investigate and develop the necessary improvements that must be made to meet the national cost targets. The outcomes expected from this project include the development of novel processes and materials for making step changes in the cost of emissions controls, and an understanding the potential cost savings associated with integrated emissions relative to conventional power plant emissions controls.

While the primary focus of this project was to develop new emissions capture processes, there were also several foci to build internal capabilities as well as understand the global technical and economic realities of emissions capture:

- Analysis of existing domestic coal power plant fleet.
- Competition for new builds (both for retirements and base load replacement due to CCS parasitic loads).
- Past experience with emissions capture development (cost migration) and comparison to the effort required for CCS.
- Definition of the cost of electricity (LCOE) and relative impacts of components and financials.
- Weighting of factors that impact the LCOE.
- Economics of current reference CCS flowsheet by plant area.
- Understand all sources of heat in typical power plants to identify "free" energy that does not impact or minimizes the impact to the steam cycle.
- Life cycle analysis (LCA) to understand the magnitude of environmental impacts resulting from different emissions capture options.

Life Cycle Analysis. The implementation of carbon capture and storage will have many social, economic, and environmental impacts beyond greenhouse gas emissions that must be considered to achieve sustainable energy generation. To understand the full impact of CCS, we must look beyond the boundaries of the power plant and understand the impacts on increased waste disposal, coal mining, coal transportation, and the like.

LCA of power generation processes utilizing CCS technology via the MEA absorption process were reviewed as well as those of other energy generation technologies as applicable. The variability between studies can be quite large, even for core metrics of performance such as the reduction in GHG potential. Nonetheless, a few key areas of impact for CCS emerged from the studies reviewed:

1. The impact of MEA generation on increased eutrification and acidification from ammonia emissions and toxicity from MEA production.
2. The impact of increased coal use, resulting in increased generation of nitrogen oxides, decreased energy efficiency which could impact the economic sustainability of the program, as well as related impacts due to increased mining of coal and limestone and disposal of toxic fly ash and boiler ash waste streams.

3. The impacts from carbon sequestration, which are small compared to first two categories, but uncertain due to the risk associated with different sequestration strategies. These impacts include acidification of water (groundwater, oceans, or aquifers, depending on sequestration site), social and human toxicity impact (if large release from pipeline or wells), and the legal and public policy risk associated with licensing CO_2 sequestration sites.

In addition to identifying potential environmental, social, or risk-related issues that could impede the large scale deployment of CCS, performing LCA-based studies on energy generation technologies can suggest places to focus our efforts to achieve technically feasible, economically viable, and environmentally conscious energy generation technologies for maximum impact. Sustainability assessment is a tool that uses inputs from both LCA and TEA to allow for the comparison and analysis of the trade-offs between environmental, social, and economic impact categories and metrics. This type of analysis of direct and indirect impacts should serve as the basis for defining energy policy priorities and research directions at the plant site as well as upstream, downstream, and integration facilities.

Preferred candidate technologies. Over 80 technical ideas were generated and evaluated. The top candidates were as follows:

- PNNL's CO_2-Binding Organic Liquids (CO_2BOLs) with Polarity-Swing Assisted Regeneration and heat pump integration
- Cryogenic acid gas separation
- Hot oxy-combustion for high electrical generation efficiency
- Use of heat pumps to upgrade low-grade plant heat for use in CO_2 capture
- Natural gas combined cycle with advanced CO_2 capture/ co-gen with coal plant
- Biomimetic acid gas capture
- Pure oxygen generation using magnetic separation
- PNNL's electrochemical/pH swing technology
- Integrated fuel cells into power plant to utilize waste heat for carbon capture system
- Geothermal energy for solvent regeneration
- Combined power/Fischer Tropsch plant with heat integration.

The top candidate, PNNL's CO_2BOLs using polarity swing regeneration and heat pump, is a good example of integrated emissions and has significant promise to meet DOE's cost goals. The novel binding organic liquid is a significant improvement on the current baseline MEA solvent, but it alone does not allow the necessary cost reductions. However, the low regeneration temperatures of the proposed technology also allow a unique energy integration method that can reduce overall parasitic loads by more than 65% compared to commercial systems and reduce the cost of electricity impact for CCS from 86% for the current commercial offering to 44% for the CO_2BOLs system. This is a significant improvement and approaches the DOE goal of 35%.

Modeling of Distributed Energy Resources in the Smart Grid

Shuai Lu, Marcelo A. Elizondo, Karanjit Kalsi, George Chin, Maria Vlachopoulou, Ebony T. Mayhorn, Nader A. Samaan, David P. Chassin, Jason C. Fuller, Forrest S. Chassin

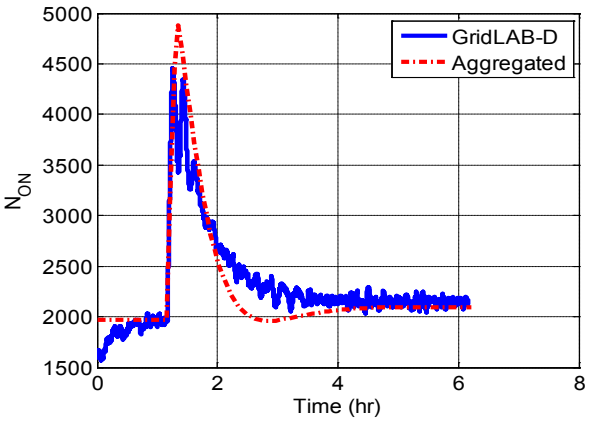
◆ This project will develop generic models for distributed energy resources (DER) in the smart grid, including distributed generation, distributed energy storage, and demand response. ◆

To build a more reliable, efficient, and sustainable power system, the transformation into the smart grid must emphasize distributed resources, featured by local controls and responses at each device to real-time price signal, system frequency, and system voltage or their derivatives. Distributed energy resources will reduce the peak capacity requirement on generation and transmission assets, improve survivability of subsystems during severe disturbances at the interconnection level, and solve the intermittency issue associated with high penetration of wind and solar energy. Extra controllability gained through distributed energy resources may not bring benefits unless they are properly designed and their effects on the system understood and predictable.

This project is developing aggregated models that will represent the dynamic or steady-state characteristics of DER in distribution and transmission system studies, providing essential components for design, planning, and operation of the smart grid. The work requires knowledge on power systems, power electronics, control theory, and computational and statistical techniques. Developing DER aggregated models and making them available to scientists and engineers will remove technical barriers, reduce the repetitive work for each DER-related study, and speed up design and implementation.

Our main challenge is to model the aggregated behavior of populations of thousands of DERs in response to frequency, voltage, and price signals. In FY 2011, we started with detailed models of DERs in a distribution system that was used for initial validation of aggregated models to gain insight in the basic behavior of populations of DERs. We explored analytical and stochastical modeling approaches to develop aggregated models for planning and operational studies, showing interactions between DER populations in distribution systems and large generators in the transmission grid.

We made significant progress in developing two approaches for aggregated models of demand response and in developing detailed model of DERs in a distribution system. We leveraged the capability for a detailed model of DER developed in another project that built major house load models. The A/C unit, electric water heater, and battery storage charge and discharge models were further developed and validated to achieve better accuracy. Photovoltaic and wind turbine models were improved to solve instability issues in some situations. A testbed for distribution systems with DERs is complete and ready for steady-state and dynamic responses.



Result of aggregated state transition model and detailed simulation of 10,000 building models.

Two approaches are being developed to derive the aggregated models for thermostatically controlled loads (TCLs): Dynamic Bayesian Network (DBN) and the state transition (ST) model. In the first approach, DBN uses training data obtained from simulation of detailed models to get an appropriate model structure and its parameters. Then, the structure and parameters are adjusted using expert knowledge of physical models and test data. In real-world applications, training data are expected to come from historical data accumulated from operations (e.g., a load aggregation company operating a large amount of demand response). The trained DBN will help estimate the availability of resources and the response after control actions are applied. In the second approach, ST model aggregates the TCL devices being modeled into a few states. The transition of the devices between these states, caused by either environmental parameters or control actions, is simulated and transition rates are calculated. Based on the number of devices in each state, the total power consumption of the devices can be estimated. Simulation results of the aggregated model were compared with that from the detailed model to validate its correctness.

In FY 2012, the two approaches for aggregated load models will be further developed. The emphasis will be building scalable aggregation models, or multi-scale physical representation of the distribution system with DERs. Multi-scale time domain simulation has also been added to the scope of this project.

New Adsorbent Materials for Desiccant Cooling

Daryl R. Brown, Praveen K. Thallapally

◆ This project will result in physical and thermodynamic data for water adsorption with metal organic frameworks (MOFs) and concepts for utilizing these materials in more effective desiccant cooling systems. ◆

Space cooling is usually one of the top two energy loads in residential and commercial buildings. For most U.S. applications, latent cooling associated with dehumidification is a significant fraction of the cooling load. Thermally driven desiccant cooling systems are an attractive alternative or supplement to vapor compression cooling in locations where low-cost thermal energy is available (e.g., from distributed generation equipment) and/or when space cooling is provided by relatively inefficient air-cooled vapor compression technology. The use of MOFs-based materials is an active area of interest for gas separation applications, but relatively little work has been focused on using these materials for desiccant applications, even though these materials are known to adsorb large quantities of water. Detailed analysis on sorption capacities and heats of adsorption and desorption of water molecules will provide critical information about the suitability of MOFs as alternate to silica gel.

This project will develop additional physical and thermodynamic data for water adsorption with MOFs and concepts for using these materials in more effective desiccant cooling systems. If laboratory results and conceptual engineering and economic analysis continue to indicate promise, this research capability would lead to the development of prototype equipment around the best candidate MOFs. Specifically, we expect to be able to determine cost and performance characteristics of the candidate MOFs compared to incumbent desiccants to determine the best one or two, determine the MOF heat capacity and density, and develop a conceptual design for a MOF-based desiccant dehumidification system. By the end of the project, our results will enable us to determine whether prototype development and testing is warranted.

Over 10 sorbents were synthesized and characterized during the past fiscal year for desiccant applications. All the MOFs synthesized show an outstanding water loading at relatively low partial pressures. Compared to silica gel – the incumbent commercial desiccant material – test data indicate a faster adsorption rate, lower regeneration temperature, lower regeneration energy, and higher equilibrium loading. Following are only the MOFs that show the significant water loading at room temperature.

Syntehsis of mesoporous MOF (MIL-101). A solution containing $Cr(NO_3)_3 \times 9H_2O$, 1,4-benzene dicarboxylic acid (H_2BDC), hydrofluoric acid, and de-ionized water (7.5 ml) was filled in a 25 ml Teflon liner. After autoclaving, heating, and cooling, the reaction mixture was washed with hot ethanol five times to eliminate excess recrystallized dicarboxylic acid. The product was separated from water/ethanol by using a small pore fritted glass filter and dried at reduced pressure overnight to obtain activated MIL-101. Similarly, another mesoporous MOF was obtained from a mixture of $FeCl_3 \times 6H_2O$ and trimethyl 1,3,5-benzene-tricarboxylate dispersed in 5 mL of water being heated for three days in a Teflon-lined autoclave. The orange solid was recovered by filtration, washed three times with acetone. Finally, the material was dried at reduced pressure overnight to obtain activated MIL-100Fe. Powder x-ray diffraction of MIL-101 and MIL-100Fe were reported to have no pattern changes in the powder x-ray during activation and water uptake experiments, indicating great stability of the sorbents and suitability for recycling.

Water Uptake (%) Summary

MetalO	Linker				
	DHTA	Imidazole/trizole	BDC	BTC	-CN
Mg	70				
Ni	50				
Zn	-	35-40		55	
Co	45				
Cr	-		90		
				72	
Cu				60	
NiCo					35
CoCo					30
MnCo					28
ZnCo					27
FeCo					35

Water uptake in various MOFs at room temperature and P/Po = 0.5. Water loading in silica gel is 25 wt% at P/Po = 0.5.

Suitability of sorbent materials for desiccant applications. The water sorption kinetic studies were carried out at for MIL-101Cr and MIL-100Fe at different humidity conditions. Following activation, MIL-101Cr was exposed to air under controlled temperature and humidity and different aliquots of the same sample were collected at different times and analyzed. TG-MS was carried out on each sample by heating to a final temperature of 500°C. MIL-101 was reused several times by activating back the material, which shows higher water adsorption values at higher humidity. More importantly,

there is a five-fold increase in water uptake at long (> 90 min) exposure times when humidity is 98%. In addition, the water uptake increases at a significantly higher rate in the first few minutes compared with water sorption at lower humidity levels. These results have a strong correlation with the isotherms obtained using pure water vapor at room temperature. The isotherms show a relatively low uptake at relative pressures below 0.5 (equivalent to a humidity level of 50%). Above this relative pressure, the isotherm shows a large step which it is related to a phenomenon called “open gate” mechanism where at a given pressure the material shows a rapid increase in surface area and water capacity.

MIL-100Fe was activated and exposed to 60% and 98% humidity levels. Exposure times were varied from 2-120 min, at which time the sample was analyzed using TG-MS using identical heating conditions to those employed for sorbent MIL-100Fe. There is a nearly twice increase in water uptake at long (> 90 min) exposure times when the humidity level is 98%. Further, the water uptake increases at a faster rate when going from lower to higher humidity levels. The isotherm shows a nearly linear increase of water sorption with relative pressure and the numbers at low P/Po (0.2 equivalent to 20% humidity) correlate well with the water uptake in the presence of air at low (23%) humidity values. However, at higher water vapor partial pressures the water uptake values in the pure water isotherms are higher (55%w/w at P/Po = 0.6 and 75%w/w at P/Po = 0.95) than the water sorption values obtained when exposing the sample to air with 60% and 98% humidity (water uptake 35 %w/w and 65% w/w, respectively).

Based on the data obtained, several MOFs were shown to have significant water adsorption at relatively lower pressure with improved kinetics and low heat of desorption. We believe these materials could potentially replace the existing materials in the desiccant industry. We initiated discussion with various industries for possible funding to develop further and demonstrate MOFs as alternate desiccant materials.

Novel Carbon Capture Materials

David L. King

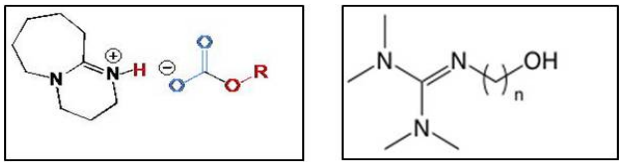
◆ This project will develop analytical capabilities to quantify the amount of CO_2 taken up and released, along with determining the heat of adsorption of $CO_2$with solid absorbent materials. It is envisioned that this capability can be applied to both internally developed materials and materials that might be provided by others. ◆

The use of fossil fuels for power generation, especially with large, coal-based plants, has the potential to impact the world climate adversely through generation of greenhouse gas CO_2. Major efforts in various laboratories have been devoted to carbon capture and sequestration to mitigate the effect of this CO_2 generation. The most costly aspect is the actual selective capture and release of CO_2 (as opposed to storage). For this reason, minimizing the cost of CO_2 recovery is a significant driver in technology selection. Our overall goal is to develop a portfolio of novel, cost-effective, material-based approaches for CO_2 capture, primarily from coal-based power plants where it is present in flue gas. Our work supports investigations of leading candidate materials (solids and liquids) for CO_2 capture from post-combustion processes (such as coal combustion) in pulverized coal power plants. In particular, we support development efforts for specifically formulated ionic liquid-type solvents (COBOLs), electrochemically driven pH swing CO_2 capture, hydrophobic solid materials to allow separation of H_2O from CO_2, and next generation oxygen looping combustion materials in which CO_2 is obtained in the absence of competing gases.

In addition, we have supported analytical developments aimed at assisting the implementation of a technical readiness level (TRL) gate analysis as a means to distinguish promising from not-so-promising carbon capture technologies. Thus, an additional goal has been development of analytical capabilities to generate measurements that can be supplied to the TRL. This analysis identifies technical requirements that must be met in order for a technology to advance to the next level. For comparison, each technology is compared against the industry standard mono-ethanolamine (MEA) solvent technology. The ultimate goal within DOE is a 70% reduction in the cost of carbon capture and sequestration relative to MEA.

Several approaches are being investigated for CO_2 capture. First, the medium may be either a liquid or a solid. Liquid capture systems are practiced in industry, with the current standard from flue gas using MEA solvent. The advantage of the liquid system is that it is easy to move the solvent from the point where CO_2 is absorbed to the point where it is released. However, the energy penalty with CO_2 release with MEA is significant, as the system retains water that is not involved in absorption (it is present to retard corrosion) but must be heated when CO_2 is released. Non-corrosive solvents with high CO_2 capacity and low binding energy are most attractive. Solid systems are much less developed for CO_2 capture. Moving solids are more challenging than moving liquids, and it is more difficult to heat a bed of solid material rather than liquid. The primary incentive for using solid absorbents is the potential for lower heat capacity so that the energy required to raise a solid absorbent to regeneration temperature may be less than the corresponding liquid.

In FY 2011, we continued support of two investigations that had been funded during FY 2010: CO_2-binding organic liquids (CO_2BOLs) and pH swing CO_2 capture in aqueous medium. We also initiated support of two other investigations: development of a modified Metal Organic Framework (MOF) material to render it hydrophobic (because H_2O adsorption competed with CO_2 adsorption) and investigation of materials that had been developed in the solid oxide fuel cell program for oxygen looping combustion. Oxygen looping combustion allows fuel combustion without air using oxidizing solid materials, resulting in a clean effluent gas comprising nearly exclusively of CO_2, rendering the capture process substantially less complicated.



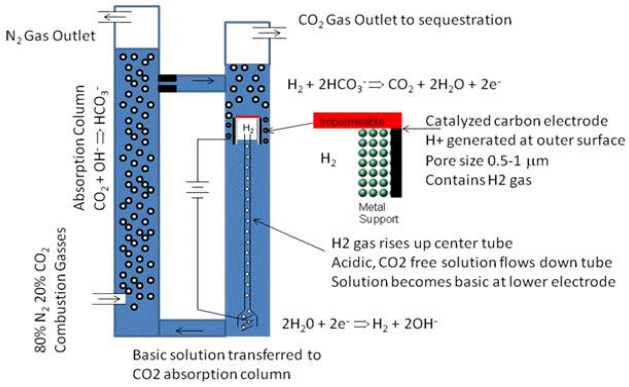
Left: first generation CO_2BOL; right: second generation CO_2BOL.

CO_2-Binding Organic Liquids (CO_2BOLs). At the end of FY 2010, two-component CO_2BOLs had good CO_2 capacity but unacceptably high volatility that would lead to solvent loss during regeneration. The resolution to this problem was seen in developing a single component BOL (second generation). Key data gained in FY 2011 included first generation (two component) BOL isotherms, viscosity data, and synthesis of non-viscous second generation (single component) BOLs. We also developed a polarity swing assisted regeneration process (PAR) and carried out engineering design (heat pump integration) and scaleup synthesis of target second generation BOL. Isotherms were measured on the wetted-wall column on a first generation DBU/1-hexanol BOL. Data measured included CO_2 flux and equilibrium loadings. We discovered that the flux appears to

slow down as temperature increased, which is the opposite of other aqueous systems.

Viscosity data of first gen BOL was measured and the data indicates a BOL with 9 wt% CO_2 load is below 20 Cp at 45°C. This suggests that viscosity of first generation BOLs can meet heat exchanger restrictions and sets a threshold for design of second generation BOLs. Second generation BOL has been made, and scale-up and viscosity testing will be completed by year's end. Absorption isotherms are sigmoidal and appear to follow a two-step chemical reaction unlike aqueous amines.

Electrochemically Driven pH Swing. An electrochemical aqueous-based method for capturing CO_2 from flue gas streams was developed and tested for proof-of-principle at the laboratory scale at the end of FY 2010 (see process schematic). For FY 2011, a preliminary analysis of the concept was carried out, as applied to a large-scale power plant. It was estimated that the flow will be slightly larger (1.4X) than that of the MEA system, so the footprints should be similar. An analysis of the pH conditions at the anode and cathode revealed that the system could operate at pH 8.2 at the anode and at pH 6.0 at the cathode, resulting in a thermodynamic overpotential of only some 55 mV. Kinetic overpotentials are expected to be more important.



Schematic of the pH swing electrochemical CO_2 capture process.

The main observations from experimental work in FY 2011 included the following:

- An electrolyte of 0.5M K_2SO_4 promotes better electrode kinetics than 4M KCl, but the limited solubility of K_2SO_4 will result in greater ohmic losses, requiring careful reactor design.
- A membrane-based, fuel cell type H_2 pump showed low overpotentials, which is consistent with literature values and a purely aqueous solution system that tended toward low overpotentials. This allowed us to conclude that there is no essential technical barrier to the concept.
- A variety of experiments using fuel cell type gas diffusion electrodes occasionally worked well and showed low overpotentials, but more often (even with identical electrode configurations) showed large overpotentials. Flooding of the electrodes appears to be the primary issue to be addressed in future work.

Fluorinated Molecular Organic Framework (MOF) Solid Adsorbents. MOFs are interesting materials with high adsorbent capacity. They have been touted for performance in CO_2 capture processes; however, the large H_2O adsorption capacity restricts the actual CO_2 measured uptake. Thus, there was interest in developing a hydrophobic MOF based on fluorine modification of conventional MOF materials. An experimental study of CO_2 and H_2O sorption measurements of isostructural fluorinated and non-fluorinated MOFs has yet to be reported. The approach to generation of a "hydrophobic" MOF was to surround the metal centers with perfluorinated groups that would provide hydrophobic properties and at the same time block access to the metal functions. This perfluorination was to be carried out as a post-treatment of a non-fluorinated MOF, Ni-DHTA (di-hydroxy terephthalic acid) MOF.

A first batch was synthesized and showed that CO_2 capacity was unchanged compared with the non-fluorinated precursor, and the H_2O capacity was decreased by a factor of two, showing directional progress. However, on re-measurement, the CO_2 capacity had decreased, indicating possible instability of the material. One possibility is that the materials are not stable in high relative humidity environments. A second sample was synthesized, and the fluorinated material showed again no decrease in CO_2 capacity relative to its non-fluorinated precursor, but also no decrease in H_2O capacity. This approach was abandoned at that point. Although alternative approaches to the generation of hydrophobic MOFs can be envisioned, they are all viewed as being too expensive. Therefore, further support of MOF materials for CO_2 capture was terminated.

Attrition-Resistant Oxygen Looping Materials. This research aims to overcome the limitations of the identified oxygen carriers and develop more robust oxide carriers using high temperature SOFC ceramic materials with the perovskite-, fluorite-, or pyrochlore-type structures. Low-cost (the ore grade) oxygen carriers will offer superior thermal and mechanical properties and provide a greater lifetime without sulfur and carbon impurity issues and accelerate CLC technology towards commercialization and deployment. Testing of these materials for both methane and syngas oxidation was demonstrated in FY 2011.

Thermoanalytical (HIDEN) Testing of Adsorbent Materials. In FY 2010, a large focus of this effort was to provide reliable measurements of adsorption isotherms for CO_2, H_2O, and N_2 for a number of candidate materials. Not only was this useful

for characterizing certain candidate CO_2 adsorbents, but this was also done to demonstrate a capability that could be advertised outside the laboratory in the area of carbon capture. In FY 2011, the efforts at obtaining adsorption isotherms continued, but in addition a second capability of the apparatus was applied to the various sub-projects: the ability to measure adsorption via a flow-through process to enable competitive adsorption (incorporating one or more gases at a time) as well as measure adsorption kinetics and determine space velocities, reactor volumes, and bed utilization. These data were further applied to the gate analysis described above, and reported at a recent technical conference.

For FY 2012, we will be examining very closely the potential for our project in CO_2 capture via pH electrochemical swing to meet certain technoeconomic milestones. Support for laboratory work on this project will be predicated on meeting these milestones. We will complete our stage-gate analysis for two technologies – COBOLs and amino-functionalized SAMMS – aimed at demonstrating to DOE an important methodology that will add credibility of our efforts in CO_2 capture to provide unbiased evaluations. We intend to support a couple additional seed projects that we believe have both high technical merit and potential for development for further funding, selected among the areas of CO_2 capture, attrition-resistant materials, and oxygen-nitrogen separations. This project will also interface with another project that involves materials scale-up and cart test and demonstration.

Operation and Process Optimization of Gasification and Carbon Capture Test Facility

James E. Cabe, Mark D. Bearden, Brian K. Boyd, Douglas J. Reid

◆ The capabilities of the testing platforms enable the effective research and advancement of proof-of-principle concepts related to the clean-up of coal derived syngas and the cleaning and capture of combustion-based flue gas constituents. Used in conjunction with the TRLGate materials development methodology and the cart-based sorbent/solvent systems, engineering-scale test platforms enable empiric evaluation of carbon capture materials using coal-derived flue gas in a realistic setting. ◆

The benefits of research-level gasification technologies for solid feedstocks have not yet been adequately leveraged. The primary issues limiting development include sheer size, lack of operational knowledge as it relates to the durability of materials, and lack of operational flexibility. The pilot-scale facility will be operated with the expressed intent of providing realistic syngas conditions and constituents to the variety of downstream processes under evaluation. Due to size and flexibility, the gasifier may be operated in fuel-rich combustion, oxy-combustion, and pre-combustion modes depending on the needs dictated by operational targets and downstream processes being evaluated.

Our test facility project and ensuing research objectives align with national goals regarding clean fossil energy and carbon management strategies. We focused on the development and operation of reliable fossil-based engineering scale pre-combustion and post-combustion testing platforms. The gasification and combustion platforms provide for continuing research into clean coal technologies and carbon capture, offering viable solutions to reducing the traditional emissions associated with the combustion of coal and providing a demonstrated pathway to the capture of CO_2. There are three primary objectives of the project: advancing the gasification platform to produce realistic syngas at atmospheric conditions targeting research objectives for hot syngas clean-up and refractory degradation evaluations; design and commission a fuel flexible coal combustion unit including flue gas conditioning equipment targeting research objectives for CO_2 capture using liquid and solid sorbents; and the development of a flue gas conditioning and testing platform at a regional 600 MW sub-bituminous pulverized coal fired power plant targeting research objectives for carbon capture sorbents and solvents.

The project team reached several milestones in FY 2010, advancing both gasification and combustion platforms. We addressed mechanical constraints in the gasification platform by re-engineering the fuel feed system, and burner nozzle. The modifications resulted in successive increases in both length of run, and overall carbon conversion as calculated. Specifically, we re-designed the fuel feed system to be capable of overcoming backpressure developed in the burner nozzle at the point of combustion, and we were also able to address flame impingement and refractory degradation at the burner nozzle by modifying the location and direction of oxidant (oxygen) feed. As a final measure, we made sure that the appropriate refractory was placed in the gasifier vessel at the time of replacement and increased the residence time, which improved carbon conversion.

In FY 2011, the project team advanced all three objectives as previously outlined, and a summary of our accomplishments is included below.

Gasification. We were provided coal derived syngas to research working to characterize the constituents and contaminant level present in the fully quenched syngas. The unit was designed and operated as a full quenching gasifier; the exit temperature at the syngas extraction location enabled flow throw analytics to be conducted using

The PNNL Flue Gas and Carbon Capture Test Facility located at the PGE Boardman pulverized coal plant. The slipstream platform provides in situ sampling of flue gas at 30 lpm for carbon capture material research and development.

conventional laboratory equipment. A final analysis of syngas indicated approximately 29% hydrogen, 23% carbon monoxide, and 1% oxygen, with the remainder as non-condensable. The testing also validated a previous estimation that carbon conversion would be compromised due to design limitations; this was determined to be range from 25 to 30% total carbon conversion.

The gasification unit was cleaned and dismantled at the off-site location and placed into storage on site for further use, when appropriate. To assist with future viability and repowering, none of the instrumentation or controls has been removed from the panel.

Combustion unit. The project team installed and commissioned a 20 pound per hour combustion unit and the supporting fuel, safety, and emission systems. Test runs were conducted to baseline and evaluate flue gas conditions from the cyclone type combustor. The project team executed combustion tests on pelletized biomass that had been pulverized to approximately 50 mesh (300 μ), pulverized bituminous coal (200 mesh), and several blended percentages of biomass and coal. The baseline combustion tests were compared against other known technologies. The project team modified the emission system(s) to reduce excess air ingress, and is considering further modifications to the burner itself to accommodate a potential need for lower excess air combustion profiles.

PGE Boardman flue gas test platform. The project team designed, built, and commissioned a flue gas extraction and conditioning platform at a regional 600 MW pulverized coal fired power plant in support of carbon capture materials research and development. The PGE flue gas test platform represents a safe and reliable source of sub-bituminous derived flue-gas. Uniquely configured, the test platform provides varying degrees of gas flow, composition, and temperature to downstream research instrumentation and equipment. Additional advantages include the emissions profile of the plant; it currently has limited controls with respect to sulfur, mercury, and other criteria pollutants providing the widest possible unbiased source of flue gas for use in materials research.

The project enables PNNL to work closely with the regional leader in pulverized coal combustion, bridging the critical gap between bench scale analysis, and significantly more capital intense pilot scale testing capabilities.

Photoelectrochemical Flow Battery

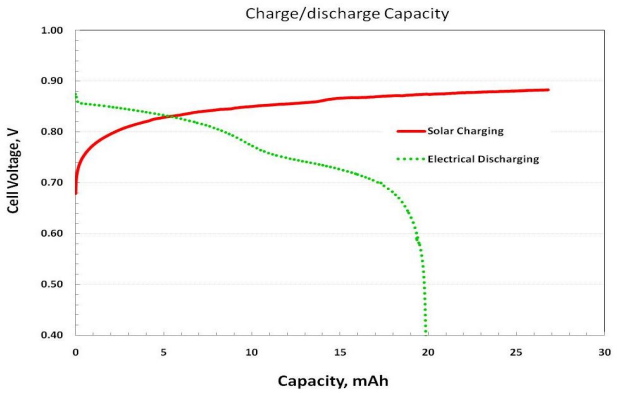
Guan-Guang (Gordon) Xia, Cheng Huang, Birgit Schwenzer, Xiaoliang Wei

We propose to develop a novel photoelectrochemical flow battery (PEB-FB) system for solar energy conversion, storage, and use. Success of this project will demonstrate a new capability to cost-effectively utilize solar energy and make valuable contributions to reduce the dependence on fossil fuels and to cut the carbon footprint for the enormous energy demand of the world. ◆

This project will develop and demonstrate a novel PEC-FB system for integrated solar energy conversion and storage. With this novel system, solar energy can be directly and continuously converted into electrochemical energy and stored in two paired flowing redox electrolytes in scalable storage tanks without an intermediate photovoltaic conversion step. The stored energy can be readily released as electricity through the flow battery system. This system has the potential to reduce materials and fabrication costs significantly and achieve up to 20% full cycle efficiency for total energy conversion and storage. To achieve these goals, we will demonstrate proof-of-concept of a laboratory-scale PEC-FB device with reasonable energy conversion efficiency, develop highly efficient photo-electrodes through materials synthesis and engineering innovation, and investigate suitable redox electrolytes and solvents with optimal properties for understanding solid/liquid interaction, charge transfer kinetics, and corrosion mechanism to achieve maximum energy conversion efficiency and extended system life.

In FY 2010, we established a testing platform by constructing conceptual photoelectrochemical flow cells and prove the novel concept by selecting suitable photoelectrodes and redox couple solutions. We screened a variety of semiconductor materials for photoelectrodes, including single crystalline silicone, gallium arsenide (GaAs), cadmium selenide (CdSe), cadmium sulfide (CdS), indium phosphide (InP), and thin films such as tungsten diselenide (WSe_2) and cadmium telluride (CdTe). Metal oxide semiconductor materials such as TiO_2 and ZnO nanoparticles were also investigated in parallel for dye-sensitized flow cells. Though most semiconductor materials for photoanodes are unstable in aqueous electrolyte solutions under illumination, we learned that they can show reasonable performance and stability under continuous flow conditions.

We discovered a new system for developing PEC flow batteries that has a ~1.1 V (fully charged) open circuit and over 75% round-trip energy efficiency (electrical charge-discharge mode) and demonstrated good stability over



A typical solar charge/ electrical discharge profiles for a CdSe (Pt)/ Fe-polysulfide/ graphite PEC-FB system under AM1.5 stimulated solar illumination.

60 cycles with nearly 100% columbic efficiency (some optimization required).

In FY 2011, we continued screening high performance photoelectrodes (especially photoanodes) based on the aforementioned new flow battery system. We worked synthesized and fabricated highly stable semiconductors, improving their energy conversion efficiency by modifying compositions and structures. We found that CdSe as the photoanode was rather stable in aqueous electrolyte solutions containing iron species. With a small amount of additives into the solution, the photoelectro-chemical solar cell performance was significantly improved (over 8% energy conversion efficiency). Using a modified single crystal CdSe photoanode, we successfully demonstrated a proof-of-concept PEC-FB system with an initial solar energy conversion efficiency of 1.7%, although it requires modification due to high cell resistance and low photocurrent.

From this recent work, we discovered a novel method for directly growing large-area of WSe_2 thin films with oriented crystalline nanowires that have potentially high photo-energy conversion efficiency and excellent stability. Preliminary data imply that the new photoanode materials are very promising. Under simulated AM1.5 illumination and flowing redox couple electrolyte solutions, the solar to electrical conversion efficiency of the operating thin-film WSe_2 flow cell is 8.2%.

For FY 2012, we will further optimize the CdSe-based PEC-FB system to improve its performance and modify fabrication processes to obtain high quality nanowire WSe_2 thin films. We will also explore flow dye-sensitized/quantum-dot-embedded solar cells with improved efficiency and stability. Finally, we will strive to understand the obstacles for increasing conversion efficiencies and extending system life.

Quantify the "State of Health" of Nuclear Structure/Materials with an Inverse Resonance Inspection Algorithm

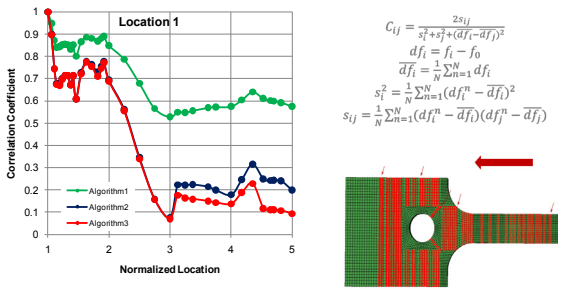
Canhai (Kevin) Lai, Xin Sun, Wei Xu, Charles H. Henager Jr., Leonard J. Bond

◆ Our research will build a unique suite of experimentally validated computational algorithms to correlate inversely the measured, real-time structural acoustic spectra to the possible degraded state of nuclear structure/material. ◆

Nuclear energy is an important element for increasing our Nation's clean energy portfolio for environmental friendly sustainable growth. Currently, the existing U.S. nuclear reactors account for at least 70 percent of the low greenhouse gas-emitting domestic electricity production. Though the existing U.S. nuclear fleet has a remarkable safety and performance record, many of the reactors are approaching their designed life spans. However, because DOE's R&D Report to Congress identifies the development of "technologies and other solutions that can improve the reliability, sustain the safety, and extend the life of current reactors," non-destructive structure condition monitoring techniques must be developed to quantify the "state of health" of reactor structure materials and to predict their residual safe operating life with the in-situ quantified material properties.

The objective of this research is to build a unique suite of experimentally validated computational algorithms inversely to correlate the measured, real-time structural acoustic spectra to the possible degraded state of nuclear structure/material. We will create a unique capability addressing the above needs with the development of an integrated experimental/modeling approach using inverse resonant ultrasound spectroscopy or resonance inspection (RI). Widely used in productions, current RI technologies lack the specific means to identify the location and size of the flaws. This project involves the development of inverse algorithms, simulations of finite elements, sample preparation, and experimental RI data collection. More accurate correlation algorithms will be developed further to improve inverse resonance inspection to pinpoint structural flaws and build a prototype inverse RI algorithm software suite.

In FY 2011, we achieved several important technical milestones. We developed a computationally efficient method based on linear perturbation theory to predict resonance frequency shift of a flawed part based on the finite element analyses of a perfect part. The results were summarized in a manuscript submitted to the *Journal of Sound and Vibration*. On algorithm development, we adopted two more sophisticated correlation functions, both providing needed improvements on the accuracy of the inverse algorithm. The



Accuracy comparison of three inversion algorithms.

effectiveness of three correlation models has been evaluated and compared. Frequency shifts for a stainless steel dog-bone with local stiffness reduction at different locations are predicted with ABAQUS simulations, and are used as numerical examples. We also developed a prototype software suite that establishes virtual flaw database from the finite element method (FEM) simulation results and predicts the locations and nominal sizes of up to three flaws.

In the software suite, a maximum correlation-based algorithm for resonance inversion is numerically examined and validated, using three correlation functions mentioned above. The results demonstrated that the inverse resonance inspection approach can quantify accurately the locations of up to three unknown dispersed flaws. However, the prediction accuracy starts to decrease when more flaws exist and when the flaws are close to each other. We also identified several important links that need to be established before this inverse resonance inspection methodology can be put into engineering practice. The results of the inverse algorithms study have been summarized in another manuscript submitted to *ASME Journal of Vibration and Acoustics*. On the experimental tasks, we fabricated at least 30 structural parts and completed RI test on them. Comparisons with modeling results are underway to establish the consistency between the FEM predictions and experimental RI measurements for both perfect and flawed populations.

In FY 2012, we will further improve the inverse resonance inspection algorithm and the software suite. We will designthe sensitivity matrix and the computational algorithm utilizing the database. The matrix should consist of one or several virtual flaw databases designed with maximum orthogonality based on the geometry of the parts or structures. An iterative computational algorithm will be pursued to use the database intelligently to find flaws in different types, sizes, and shapes at different locations.

Sensitivity Analysis of Kalman Filter and Its Applications in Power Systems

Zhenyu (Henry) Huang, Pengwei Du, Karanjit Kalsi, Yannan Sun, Ruisheng Diao, Kevin K. Anderson, Yulan Li, Barry Lee

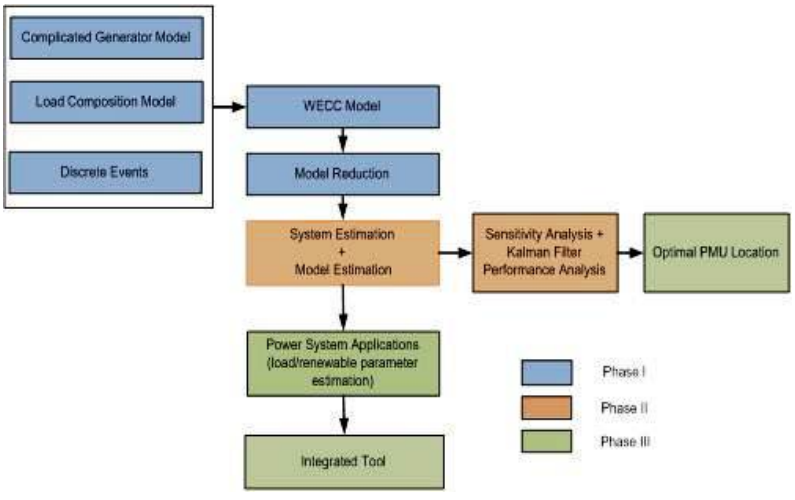
◆ We will investigate sensitivity properties of the Kalman filter and apply them to determine power grid observability and model parameter identifiability. These qualities are then used to determine optimal sensor placement and model parameter calibration, respectively. The success of this research will significantly improve the performance of dynamic state estimation and other applications in power systems and other domains. ◆

As one type of complex engineered system and one of the nation's critical infrastructures, power systems pose fundamental challenges in real-time operations and control because they are highly dynamic systems consisting of a large number of interacting elements with severe nonlinearities. Today's tools for real-time grid operations are mostly based on steady-state models with response time in the order of minutes, unable to capture the dynamic nature and too slow to prevent system failures. Tackling this challenge, recent developments resulted in the formulation of dynamic state estimation using the extended Kalman filter (EKF), which is able to estimate power grid dynamic states based on a dynamic model and high-speed sensor data such as measurement from phasor measurement units (PMU). Two of the key success factors in dynamic state estimation are the quality of the dynamic model and the locations of the sensors. Given the complexity of power grids, there are a large number of candidate sensor locations and a large number of model parameters. These locations and parameters are not of the same importance in terms of the quality of the estimated dynamic states. Identifying the key locations and parameters is an immediate need in the power grid dynamic state estimation application.

Therefore, to ensure good performance, EKF-based dynamic state estimation needs adequate sensor measurements and a good dynamic system model. This raises technical issues on sensor placement and model parameter identifiability. Both issues point to the need of sensitivity analysis of the EKF formulation. This project is on the cutting edge of the challenge to study the fundamental underlining mathematics of the Kalman filter so that we can derive the sensitivity formulation of Kalman filter and apply the sensitivity information to assess the significance of parameter uncertainty and evaluate the location value of measurements (PMUs). The resulting capability of optimal sensor placement and model parameter calibration will lead to significant performance improvement of dynamic state estimation for real-time power grid operation. The derived sensitivity property of Kalman filter is also applicable to other engineering domains.

In FY 2010, efforts were focused on developing a framework to quantify the sensitivity of the performance of the EKF with respect to different parameters to be calibrated and sensor placement. Because the Kalman filter is a two-step process, namely, prediction and correction, the proposed method evaluates the filter's sensitivity in an integrated frame. As such, it can consider the effect of all the factors such as system models, process and measurement noises. These efforts and accomplishments have significantly enhanced our fundamental understanding of how the performance of EKF relates to dynamic models and sensor placement. Thus, it enables us to implement and improve the filter's performance for large, complex power system models.

During FY 2011, research efforts have been continued in identifying the key sensor locations for the application of Kalman filter for dynamic state estimation. Because sensors and the related communications infrastructure are often monetarily expensive, or the associated estimations are often computationally expensive, our work this year proposed framework to identify the optimal sensor placement in the sense that it maximizes observability while minimizing cost. First, a new performance metric to measure system sought observability and model parameter identifiability. To evaluate the tracking results, the diagonal entries of the steady-state error covariance, $P_\infty = \lim_{k\to\infty} P_k$, are used to measure the estimation uncertainty in state variable tracking.



Application of advanced Kalman filter for power grid planning and operation.

To determine best locations for PMUs through exhausitve search is an NP-hard problem, which requires lots of processing effort, especially when the number of generators presented in the system increases. The work in FY 2011 has developed a new, scalable search algorithm for the PMU placement problem. The algorithms search for placements that give small state tracking error. The state tracking is evaluated by an EKF-based procedure. The algorithms are robust because the tracking performance is not affected by fault locations. The processing effort is significantly reduced as compared to the original optimal PMU placement problem.

We developed a distributed dynamic state estimation method using the extended Kalman filter to track the dynamics and calibrate the parameters for a multi-machine power system. High computation complexity creates significant challenges for real-time applications when a centralized dynamic state estimation is used. Therefore, a domain decomposition method has been proposed to utilize decentralized computing resources. The performance of distributed dynamic state estimation is tested on a 16-machine, 68-bus test system. Simulation shows that it is robust and accurate in terms of both dynamic state tracking and parameter calibration. Because of its unique distributed architecture, its fast computation speed makes it more suitable for real-time applications compared to the centralized implementation.

The work in FY 2011 has generated considerable intellectual properties and publications, and represents a culmination of a three-year research effort to improve the performance of dynamic state estimation for complex systems. Our completed work provides a foundation for the real application of the EKF-based dynamic state estimation for a future grid. The factors influencing the performance of EKF have been well addressed, and this discovered knowledge represents a significant step toward the fundamental understanding of the EKF and its application for large-scale complex systems.

Stabilized Li Metal Anode for Li Batteries

Jason Zhang, Wu Xu, Jie Xiao, Rick Williford

◆ Energy storage devices, especially batteries with good reliability, affordability, and environmental friendliness for plug-in hybrid electrical vehicles (PHEVs) and pure electrical vehicles (EVs) are critical for the United States. While the current lithium ion battery technology can satisfy the short-term need of EVs, a high capacity, low voltage, low cost anode is required for the long-range operation of the next generation of EV applications. ◆

Lithium metal has an extremely high specific capacity (3820 mAh/g) and a very low potential (–3.04 V vs. SHE). Therefore, it is an ideal anode for high energy lithium batteries. However, the use of lithium metal as an anode has been hindered by the dendrite growth during repeated charge/discharge process, which may lead to a short circuit and safety problem in lithium batteries. The changes in the morphology of lithium anode can also lead to increased impedance of the whole cell, as demonstrated in lithium-air batteries. Therefore, there is an urgent need to understand the dendrite growth mechanism. After 20 years of limited work in this field, the urgent need to double the energy density of batteries used for EV and new development in nanomaterials drive a renewed effort around the world to improve the stability of the lithium anode.

In FY 2011, we performed fundamental analysis on the processes of lithium dendrite nucleation and growth using an approximate quantum mechanics method electron force fields (eFF). The main results of simulation are as follows: 1) Lithium nucleation is the controlling step. Once lithium dendrite starts to grow, it grows quickly, 2) critical lithium nucleus diameter is approximately 0.25 μ, 3) subcritical lithium nanodot dissolves when its atoms are mobile, 4) no dendrite forms when subcritical nanodot atoms are "frozen," and 5) stable lithium-lithium bonds may form on "frozen" lithium film.

At the same time, we systematically investigated the effects of various electrolyte solvents on lithium dendrite growth at the surface of copper substrate during the electrochemical deposition process. The solvents were chosen from ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), vinylene carbonate (VC), monofluoroethylene carbonate (FEC), and vinylene ethylene carbonate (VEC). Lithium was electrochemically deposited on Cu surface within the same time period (approximately 15 hrs) in different electrolytes of 1 M $LiPF_6$ in the selected single carbonate solvent or mixture of carbonate solvents. Morphologies of lithium deposition films were analyzed by scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS) dot mapping and x-ray photoelectron spectroscopy (XPS). The main results of our study are listed below.

- Cyclic carbonate solvents (EC, PC, VC, VEC, FEC) lead to more smooth and uniform lithium deposition than linear carbonate solvents (DMC, EMC)
- Lithium film quality has the following order:
  - PC > VC ~ VEC ~ FEC > EC >> EMC > DMC
  - EC/DEC > EC/EMC > EC/DMC
  - PC/DEC > PC/EMC ~ PC/DMC
- Lithium deposits easily at the edges of the substrate and the places where defects exist
- EDS Dot mappings show F, C, O, and P elements are everywhere in the deposited area. XPS data also shows the existence of Li, F, C, O, and P in the deposited lithium films. The F, C, O, and P are from the reactions of freshly deposited lithium with $LiPF_6$ and carbonate solvent during deposition.

In a separate effort, we developed special membranes to minimize lithium dendrite growth. These membranes were prepared with hydrothermal crystallization method and have small pore sizes that allow the conductive ions and solvent molecules to pass through. After these membranes were assembled into cells and lithium deposition was conducted, they were analyzed by the same methods. It has been found that nearly no lithium dendrite forms at the surface of these membranes. Therefore, a zeolite membrane may be a good protection layer to suppress lithium dendrite formation.

In FY 2012, we will further investigate these novel approaches to prevent lithium dendrite formation and growth. A porous polymer film will be used as the base for a physical blocking separator. In parallel, different organic and inorganic additives will be studied in a PC-based electrolyte to further suppress dendrite formation. We expect that this combination of physical blocking and chemical passivation methods will form a reliable barrier to prevent lithium dendrite growth and used for all lithium metal batteries.

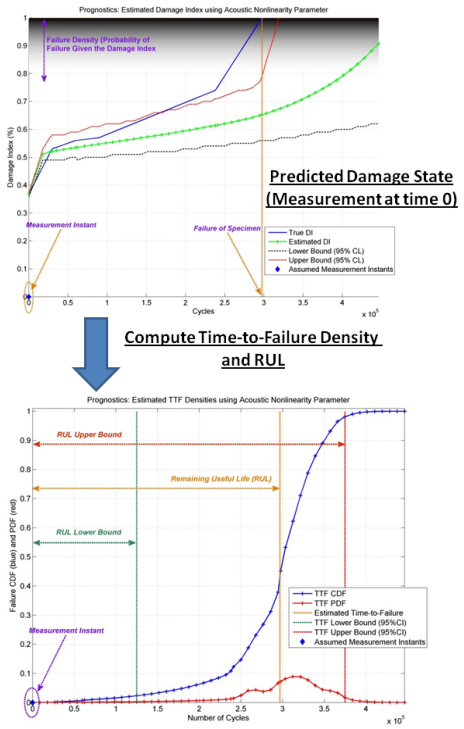
Engineering and Manufacturing Processes

Demonstration of On-Line Monitoring and Physics Based Prognostics

Pradeep Ramuhalli, Mukul Dixit, Jeffrey W. Griffin, Leonard J. Bond

◆ This project will investigate innovative sensing technologies and prognostic methods to support residual life predictions for materials subjected to stressors. The resulting capability will form the basis for advanced diagnostics and prognostics tools needed to support U.S. nuclear power plant life extension beyond 60 years, and provide novel online monitoring tools for incorporation in new advanced nuclear power plants. The methods proposed will contribute to maintaining and potentially improving the safe and economic long-term operation of legacy plants. ◆

A central issue in life extension for the current fleet of light water nuclear power reactors (LWR) is the early detection and monitoring of materials degradation due to stresses and irradiation. Related is the ability to estimate remaining useful life (RUL) of components and systems based on the degradation information. The assessment of remaining life is important in proactive- or prognostic-based life management of these facilities since such "condition-based maintenance" strategies can potentially improve safety and reduce costs by detecting damage and scheduling appropriate mitigation strategies early in the component lifecycle.



A probabilistic approach to estimating RUL from measurements of early stages of material degradation has been developed.

For early detection of material degradation, novel nondestructive (i.e., without destroying the utility of the specimen) diagnostic methods suitable for continuous monitoring over extended periods (months to years) are needed. The challenge of predicting remaining life starting from earlier phases of degradation is also largely unsolved and will require new prognostics tools. Research activities in this project are addressing these questions. The objectives of this project are to develop diagnostic methods to assess degradation in materials used in legacy LWR and prognostics algorithms to estimate RUL from these measurements.

Research in FYs 2009 and 2010 focused on the development of new diagnostic tools and prognostic algorithms. The research focus during FY 2011 was on integrating the diagnostic and prognostic tools to quantify the degradation state of mechanically fatigued ferritic steel specimens and, using this information, to estimate the RUL. Ferritic steels are commonly used in LWR components and in an LWR operating environment can develop fatigue cracking, particularly near structurally significant locations such as welds. Early stages of fatigue in ferritic steels result in changes in the material microstructure, such as the formation of dislocations and slip bands. These changes result in local variations in electrical conductivity, magnetic permeability, and elastic constants. Sensitive to such changes, nondestructive methods (such as magnetic Barkhausen noise and nonlinear acoustics) were therefore selected (during the FYs 2009 and 2010 periods of the project) for early material degradation state evaluation.

To determine the sensitivity of these techniques to early-stage damage and demonstrate monitoring of degradation accumulation, multiple specimens were subjected to interrupted tensile and fatigue tests in this phase of the project. The measurements obtained indicate good correlation with early stage damage accumulation. These diagnostic measurements were applied to a Bayesian prognostic algorithm, developed during FYs 2009 and 2010 to provide a first demonstration of integrated diagnostics and prognostics for RUL estimation in LWR materials. Results to date from this integrated laboratory-scale tool show the feasibility of RUL estimation from early damage measurements.

This project has resulted in 15 publications and four invited presentations to date, and has contributed to a draft international report through an International Atomic Energy Agency coordinated research program that is assessing advanced diagnostics and prognostics for nuclear power plants. FY 2011 was the final year of this project, and the results are being compiled into a comprehensive journal paper for dissemination to the research community.

Materials Science and Technology

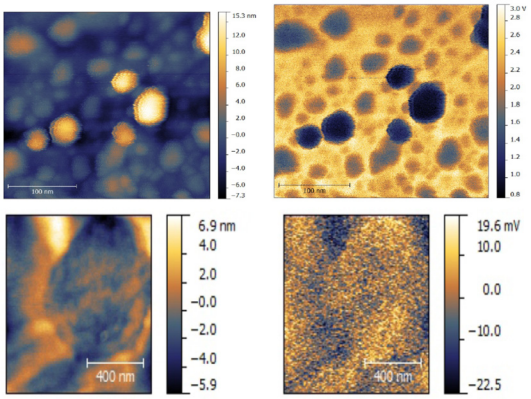
Facet Specific Chemistry of Noble Metal Nanoparticles Using an Enhanced Scattering Infrared Scattering Near-Field Optical Microscope

A. Scott Lea, Matthew S. Taubman, Mark C. Phillips,
Liang Wang, Michael A. Henderson

◆ This project seeks to integrate a quantum cascade laser with an atomic force microscope to develop a novel, state-of-the art capability in scattering infrared near-field optical microscopy to investigating the distribution of bonding configurations and heat of adsorption of probe molecules on the different crystal facets of noble metal nanoparticles. ◆

Molecular and inorganic nanostructures, polymer and supramolecular assemblies, proteins, correlated systems, and many other natural and synthetic materials gain their unique functionalities from intra- and intermolecular interaction and electron correlations on mesoscopic length scales of 10s of nm. Gaining a molecular level understanding of the materials' structure and function has remained a major experimental challenge due to the lack of techniques that routinely provide a chemically specific spectroscopic identification with simultaneous spatial resolution on the relevant length scale associated with the size and interactions of the molecular building blocks within the 10–100 nm range. There are instruments worldwide that can provide near-field infrared nano-imaging at high resolution, but except for the one recently developed by the Raschke Group, none is broadly tunable over a large spectroscopic range nor has resolution that approaches 10 nm.

This project adds a new capability to existing equipment that allows investigation of reactive sites on various faces of crystalline nanosized noble metals and the physical processes that occur in nanostructured materials. External cavity quantum cascade lasers (ECQCL) will be coupled to this instrument as a complementary infrared light source to the femtosecond OPO chain. These devices work extremely well in the molecular fingerprint region (8–12 μm), which will be of particular use in this instrument as this is where many fundamental vibrational bands are found. The rapid scanning capabilities of ECQCL in the 100s of Hz will allow infrared spectra to be taken point-by-point across the sample, allowing rapid spectral data coverage. The second advantage of quantum cascade laser incorporation is its ease of use (permitting wide-spread usage), low cost, and ruggedness.



Tapping mode height(right) and near-field optical (left) images of a test grid (top) at 1333cm^{-1} and of a PE/PEO polymer co-blend (bottom) at 1294cm^{-1} using an external cavity quantum cascade laser.

Based on discussions with the Raschke Group and the availability of quantum cascade laser instrumentation, we custom built an ECQCL with a continuous mode operating frequency range of 1260 cm^{-1} to 1400 cm^{-1} during FY 2010. We engineered the ECQCL output with beam characteristics necessary for ease of integration into the existing scattering IR SNOM system. The power output of the ECQCL determines detectability limits, is frequency dependent, and reaches a maximum of about 15 mW between 1330 cm^{-1} to 1350 cm^{-1}. To demonstrate the ECQCL integration, we identified an experimental system that had nm- to μ-size spatial variability in its infrared absorbance between 1280 cm^{-1} and 1380 cm^{-1}. Polymer co-blends composed of polyethylene and polyethylene oxide (PE/PEO) were chosen because these polymers phase separate into discrete domains when spun cast from solution. PE has little infrared absorbance over the operating range of the ECQCL laser, where PEO has a strong infrared absorbances due to the ether C-O stretch at 1280 cm^{-1}.

Phase separation of the polymers provided spatial variability in the infrared absorbance at either 1280 cm^{-1} or 1320 cm^{-1}. These co-blends were characterized using atomic force microscopy topographic and phase imaging modes. Contrast in phase images is due to differences in the interaction between the sample and the cantilever tip and in the case of the 75%:25% sample provides spatial variability on the micron-scale for this interaction. We therefore expected the images obtained in our ECQCL *s*-IR SNOM experiments to show similar contrast. We have also tested our ECQCL system using a gold pattern integrated onto a bare silicon wafer and have shown that the contrast due to the enhanced scattering of gold is readily observable.

For the C-O adsorption experiments on noble metal nanoparticles, it is critical to have laser tunability in the 4.8–5.4 μm wavelength range. After researching, we discovered that there is no commercially available ECQCL that covers this entire range, so we will need to develop a suitable ECQCL in-house. We identified a potential source for the quantum cascade laser chip and have begun to design the laser system that will need to be built during FY 2012.

Friction Stir Welding of Creep-Resistant Oxide Dispersion Strengthened Alloys

Glenn J. Grant, K. Scott Weil, Yuri Hovanski, Jens T. Darsell

◆ We are developing a cost-effective method of joining high performance oxide dispersion strengthened steels and demonstrating their high-temperature strength and both creep and corrosion resistance. The work will help to build PNNL's capabilities in high-temperature materials development. ◆

Because of their low cost, excellent thermal properties, and suitable corrosion and radiation resistances, ferritic/martensitic steels are key materials in next-generation nuclear plant designs and primary candidates for advanced fast reactor cladding/duct materials. Recently, there has been a push within the nuclear plant design community for higher operating temperatures to improve plant efficiencies. Unfortunately, the utilization of most ferritic/martensitic steels is limited to about 600°C due to a significant drop off in tensile and creep strength. It is well known that the addition of insoluble, nanoscale oxide dispersoids to these alloys greatly improves their high temperature mechanical properties and resistance to radiation induced damage mechanisms. These oxide dispersion strengthened (ODS) alloys are important materials for future reactors, but barriers need to be overcome before widespread use is possible. Two critical issues are implementing the technologies into final assemblies and the high cost of bulk ODS alloys. Joining or welding of ODS alloy components is especially problematic, as liquid phase methods such as brazing and fusion welding lead to regions devoid of dispersoids and associated strengthening effects, making joined components susceptible to failure by creep, even though the base ODS alloy is not.

This project addresses the barriers to implementing ODS alloys in several ways. We are evaluating the efficacy of a solid-state joining approach known as friction stir welding (FSW). Because FSW does not involve the formation of a fusion zone, it has the potential to produce joints that will maintain the creep and radiation swelling resistant properties of the original base ODS material. To address the current high cost of producing the ODS alloy, this project is also investigating a novel, single-step method of consolidating ODS alloy powder directly into semi-finished product form (such as tubing, rod, and plate).

Friction stir welding. In FSW, two metal work pieces are placed end-to-end, and a spinning tool is brought into contact along the common join-line, simultaneously heating both pieces through a combination of friction and plastic work energy dissipation. As the materials are heated, their flow stresses drop, and the shearing action of the plunging tool causes plastic deformation to take place. As a result, material from each work piece flows into the other, leading to the formation of a solid-state, metallurgical bond across the original join-line. For ODS alloys, our initial goal was to determine whether a sufficient concentration of dispersoids could be maintained across the weld region so that the joined part would exhibit creep strength essentially equivalent to that of the original pre-joined material.

Fully consolidated and defect-free FSWs are possible in this ferritic ODS alloy.

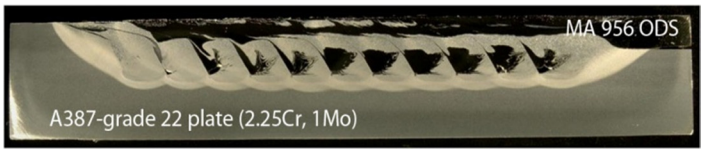
In FYs 2010 and 2011, we conducted a series of parametric welding studies on Kanthal APMT, a commercially available dispersion strengthened high chromium containing ferritic stainless steel and on MA-956, a mechanically alloyed ODS of similar composition. An envelope of successful welding conditions (e.g., linear speed, rotational tool speed, rake angle, etc.) was identified and room temperature mechanical properties were measured. Microstructural observations indicate that successful defect free welds can be made in theses material. Welds developed in this program are on 0.25-in material that are the thickest demonstrations of FSW in ferritic ODS materials to date in the open literature. Mechanical testing showed that the weldments displayed roughly the same yield and ultimate strengths as the base material at room temperature. Elevated temperature testing indicates that FSW weld metal displays the same creep properties as base metal, indicating that the welding process has preserved the unique properties of these ODS alloys.

Reducing the cost of ODS materials. As discussed, one means of increasing creep resistance in ferritic alloys is to incorporate a dispersion of fine-scale oxide particles (such as Y_2O_3). Currently, this is done by mechanically mixing a small amount of the oxide powder (typically less than 1 vol%) with a ferritic steel powder in a high energy attrition mill. Batch sizes typically are less than 1 kg, and milling times are generally between 80 and 120 hrs to achieve uniform oxide dispersion. Once the final mechanically alloyed powder is formed, it is poured into a steel can that is subsequently welded shut (after evacuating the vessel of any

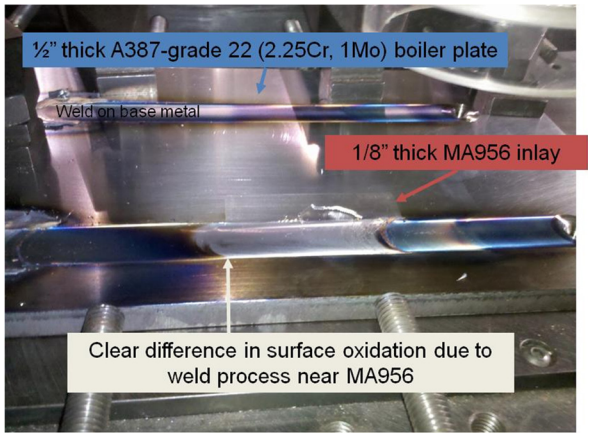
intrinsic atmosphere, such as air). The sealed can is then hot isostatically pressed (HIPed) at temperatures ranging from 1200–1750°F and 10–30 ksi. After HIPing, the densified material undergoes a series of rolling and annealing steps, followed by mechanical removal of the outer can layer, and subsequent pickling to form a final ODS sheet product. Thus, even though the raw powders for an ODS alloy cost between $1–$2 per pound, the final wrought semi-finished product ends up costing on the order of $200–$500/lb, often making ODS material too expensive for commercial application. In addition, due to the methods of sheet or tube rolling, these materials tend to display very anisotropic properties and often exhibit low hoop creep strength and poor pressure retention capability at high temperature. Rolling also often leads to the formation of larger scale oxide stringers that can deleteriously impact the mechanical properties of the final product form.

In FY 2011, we investigated direct powder-to-product methods of ODS fabrication that will eliminate many of the steps currently employed in producing these materials, generate material on a continuous (as opposed to batch) basis, and avoid property anisotropy and oxide stringering. Working with collaborators at the University of South Carolina, we demonstrated direct formation of consolidated ODS buttons measuring ~1-in diameter by 0.5-in height from MA 956 powder. TEM and XRD work reveal that the compacts are in fact composed of fully dense ferritic alloys with sub-20 nm oxides in the matrix, comparable to ODS alloys formed by much more expensive fabrication routes.

Another concept to reduce the cost of assemblies made from ODS alloys is to use the ODS alloy as a coating or cladding on a lower cost bulk material such as a boiler plate steel or reactor vessel steel therefore lowering the material cost of the entire assembly. The challenge here is that many methods used to clad a material involve melting and solidification of the clad, either melting then coextrusion or coating by one of many molten spray processes. If melting occurs, the ODS alloy will segregate the oxide dispersion and mechanical property advantages will be lost. FSW, however has the potential to join ODS plate to other substrates with a solid state joint, so all the ODS characteristics are preserved. In FY 2011, we demonstrated this concept by physically stirring a high value, but thin (0.8-in thick) ODS alloy on top of a boiler plate steel.



Cross section showing ODS alloy joined to the surface of a boiler plate steel by multiple passes of a friction stir tool plunged through the ODS plate into the chrome steel substrate. The FSP passes are into the page and each pass slightly overlaps the previous pass. In this way, the ODS is completely joined to the substarte by a solid state joint.



Oxidation discoloration is suppressed in the processed region over the ODS alloy inlay showing the concept of friction stir cladding with ODS on low cost structural materials.

The concept is to produce a creep and oxidation resistant surface composed of high value ODS alloy on top of lower cost structural steels. The picture below shows the first pass of the processing tool. The distinct change in the oxidation level of the clad surface shows the area where the FSW tool passed from boiler plate, over the ODS metal inlay, and back onto boiler plate.

Through techniques and technologies developed during the course of this project, we have demonstrated successful joining of ODS alloys, successful powder processing techniques that can lead to low-cost bulk ODS fabrication, and demonstrated new cladding techniques that can lower the cost of high performance assemblies used in aggressive corrosive, high neutron flux, or high temperature environments found in both nuclear and fossil energy power plant equipment and systems.

Identification of Damage Signatures in Advanced Reactor Materials – Exploring Design for Inspectability

Charles H. Henager Jr., John S. McCloy, Shenyang Hu, Yulan Li, Pradeep Ramuhalli, Jeffrey W. Griffin, Ryan M. Meyer

◆ This project will develop a methodology for the design of materials for nuclear reactors with an emphasis on structural materials with enhanced inspectability using nondestructive sensors. This will allow new and existing nuclear reactors to operate more safely and with greater reliability. ◆

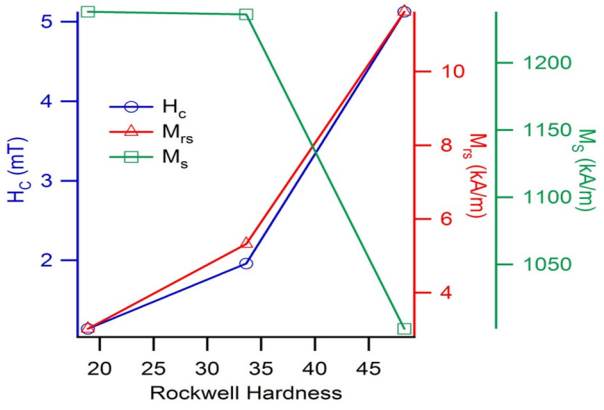
Existing U.S. nuclear reactors have a remarkable safety and performance record, and today many of these reactors are approaching their designed lifetime of 60 years. In its Research and Development Roadmap Report to Congress dated April 2010, DOE clearly identified four research and development objectives, the top one being to "develop technologies and other solutions that can improve the reliability, sustain the safety, and extend the life of current reactors." To achieve this objective, nondestructive material condition monitoring must be integrated with plant operations to quantify the "state of health" of the materials in current reactors, and more importantly, it must be used to predict reactors' residual safe operating life. One possibility of meeting this challenge is to develop new sensing techniques to monitor the integrity of reactor components. The other possibility, which has yet to be explored, is designing structural materials for enhanced inspectability.

This research will determine how to increase the signal or signatures of material damage or aging using novel methods. Our procedures will not harm the materials' desired properties so that a given nondestructive sensing technology will be better able to detect when damage or degradation occurs. This method will provide nuclear plant operators with the ability to assess the state of health of a given structure using continuous, nondestructive evaluation methods. Specifically, opportunities for designing new materials will be explored by incorporating sensing layers or specific microstructural elements into the component design and manufacturing process to make materials more amenable to continuous online inspection for advanced condition monitoring.

A specific nuclear ferritic/martensitic alloy, HT-9, was chosen for our initial study because of its magnetic signatures to determine if they could be manipulated by internal and external variables. Three different heat-treated conditions of the alloy were created with increasing hardness in alloy samples. The samples were characterized for grain size and microstructure using scanning electron microscopy as well as for hardness using standard microhardness techniques. Magnetic signatures were obtained from each condition as follows: hysteresis curves for saturation magnetization and coercivity, Barkhausen noise was determined using a PNNL custom setup, and first-order reversal curves were obtained. Magnetic Barkhausen noise results from energy required to move magnetic domains within the alloy, while first-order reversal curves measure the distribution of coercive force required to move domains.

Each of these signals was proportional in its own way to the alloy hardness, which was a very good indicator that these signals could be used to determine material degradation in a nuclear reactor since common degradation mechanisms involve radiation hardening. However, the change in the magnetic signals was small and offered great potential for enhancement through the addition of magnetic particles to the alloy. We were unable to achieve the modification in this one-year project but will reserve for the future. In addition, a computational modeling task uses an advanced phase field model to simulate the magnetic hysteresis curves of the alloy.

Future research would model the magnetic response of the alloys due to certain microstructural features that represented material damage or degradation. This would allow the model to be used to quantify the nondestructive signals based on a known amount of damage or degradation. Essentially, the model could be used to calibrate the nondestructive sensor for accuracy and reliability. This project achieved its goal of finding a magnetic signature sensitive to changes in a material property that could be enhanced by modifying the alloy by specific additions. The groundwork was paid for progress in the field so that future research can be focused on alloy modifications.



Magnetic data from the three alloy conditions shows a strong correlation between Rockwell hardness for each: magnetic coercivity (H_c), and remnant magnetization (M_{rs}). Not shown is that the magnetic Barkhausen noise decreases linearly with increasing Rockwell hardness.

In Situ Nuclear Magnetic Resonance Investigations of Trapping Mechanisms in CO_2 Storage

David W. Hoyt, Jian Zhi Hu, Romulus V. Turcu, Ja Hun Kwak, Jesse A. Sears, Kevin M. Rosso, Andrew R. Felmy

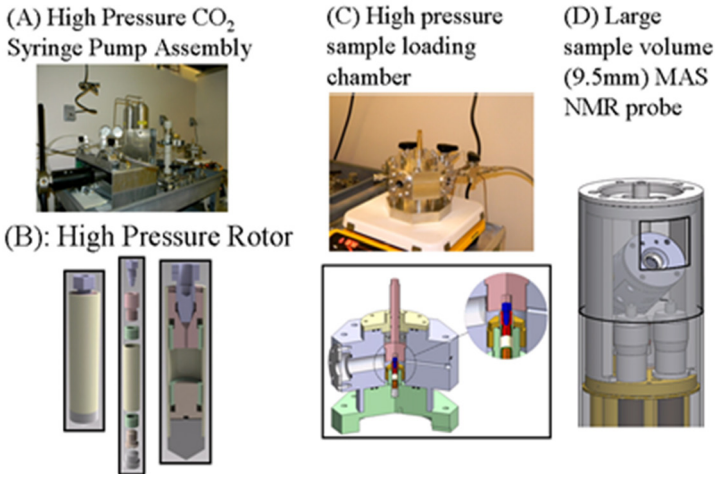
◆ We propose to develop unique in situ nuclear magnetic resonance (NMR) capabilities, including the application of existing developed techniques, to advance the understanding of geochemical processes associated with the precipitation and dissolution of CO_2 at the molecular level. ◆

Fossil fuel usage such as coal, a major source of CO_2 missions in the atmosphere, will continue to provide a significant portion of total energy in both industrialized and developing countries. It is estimated that the global emissions of CO_2 to the atmosphere would increase from 7.4GtC (Giga tons or billion tons, of carbon) per year in 1997 to 26GtC per year by 2100. Increased levels of greenhouse gases such as CO_2 are adversely affecting the global environment, as evidenced by recent trends in global warming and dramatic changes in weather patterns. These facts have made it critical to develop technologies to stabilize CO_2 in the environment.

We propose to develop and apply unique high-pressure magnetic angle spinning (MAS) NMR capability for in situ characterization of mineral carbonation mechanisms and kinetics at super critical CO_2 pressure. Our studies will unravel the role of water activity for catalyzing mineral transformation to metal carbonates, understand water activity thresholds that enable mineral transformations, uncover important chemical mechanisms involved in these transformations (dissolution, ligand-exchange, nucleation, etc.), and discover time-scales controlled by mineral transformation rates or by water availability.

In FY 2009, we designed the MAS NMR cell with nonmetals. This unique design enabled a combination of ceramics for holding the sample and plastics for high pressure sealing. Five high pressure MAS sample cells were tested for withstanding and possible leakage at increased CO_2 pressure. Results sufficiently demonstrated that ^{29}Si and ^{13}C MAS NMR were sensitive probes to investigate the detailed reaction mechanisms. During FY 2010 and after more than ten iterations, we finally achieved our goal of holding CO_2 pressure at supercritical conditions for more than 72 hours at 50°C, at higher pressures than have previously been reported in the literature. For the first time, magnesium carbonation products, reactants, and reaction intermediates were all observed in a single experiment. We also initiated comprehensive studies on the metal carbonation mechanisms and, in particular, focused on understanding the role of H_2O with other natural minerals such as antigorite and lizardite.

The capabilities performed and milestones achieved throughout FY 2011 are highlighted below.



The high pressure MAS NMR capability.

In situ High Pressure MAS NMR Capability Development. This capability consists of a special high pressure sample cell (B), a high pressure sample loading/reaction chamber (C), and a special large sample volume (9.5mm) MAS probe that provides low ^{1}H and ^{13}C background (C).

The unusual technical challenges in high pressure MAS NMR is the construction of the MAS rotor. In order for NMR to work, the rotor must be built with non-metals. However, plastics cannot be used inside the NMR RF coil because it generates both ^{13}C and ^{1}H signal. Our design is unique that enables the use of a combination of ceramics for holding the sample and plastics for high pressure sealing. Special NMR RF transmitter and receiver coil is employed to achieve the low ^{1}H and low ^{13}C background. After more than 12 iterations, we have successfully achieved our goal of holding CO_2 pressure at supercritical conditions for more than 72 hours at 50°C, where the initial CO_2 pressure was 150 bars and the ending pressure was 126.9 bars, well above critical pressure of 73.8 bars. A fully functional first of the kind 9.5 mm large sample volume MAS NMR capability has been firmly established. This capability has been applied to study metal carbonation reaction mechanisms using model mineral such as forsterite and brucite, where reaction products, intermediates and reactants and the dynamic conversion among them have been observed simultaneously regardless

whether they are in a gaseous, supercritical fluid, liquid or solid phases (either amorphous or crystalline or both).

Ex situ ^{29}Si and ^{13}C NMR investigations. The mechanisms of forsterite metal carbonation at supercritical CO_2 with water varied from dry to well above saturation, including at saturation, were investigated by a combination of solid state NMR (13C SP-, CP-MAS, 29Si SP-, CP-MAS), XRD, TEM, and XPS. We found that for a given fluid/mineral ratio there is a H_2O threshold above which a significant portion of the H_2O serves in a catalytic role where more extensive carbonation reaction occurs. Defining the role of H_2O, even in low H_2O content environments, is therefore critical to determining the long term impact of CO_2 reactivity in the subsurface. Ultimately, our research will provide new insights into the physical/chemical phenomena that underlie the carbon sequestration at the subsurface, in particular the molecular mechanisms of mineral interfacial reactions with CO_2, the effects of a varied amounts of water on this reaction, the effects of structural and chemical heterogeneity at the interfaces on the reaction kinetics, and the macroscopic dynamics of CO_2 and water at relevant geological temperature and pressure.

Integrating Multimodal Chemical Imaging Instrumentation by Data Reduction and Resolution Merge

Dongsheng Li, Guang Lin, Jian Yin

◆ This project will develop new research capabilities for integrating multimodal chemical imaging instrumentation at different resolution and length scales. The methods developed will create high-resolution images that cover large areas of a sample and provide a complete, detailed view of complex, heterogeneous structures. ◆

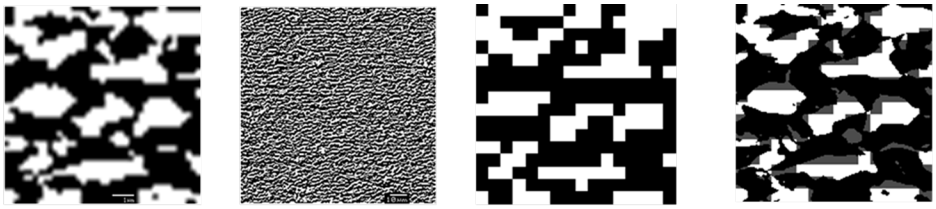
Image integration for chemical imaging instrumentation must be advanced to meet the development of large dataset generated at high speed typical in light source chemical imaging instrumentation. This trend is also observed in our in-house imaging facility development, such as high resolution mass spectrometry, secondary ion mass spectrometry, atom probe tomography, and the like. With the rapid improvement of chemical imaging facility and power of light sources, one challenge raised is how to integrate chemical imaging information obtained from different sources on multiple length scales. For example, in materials science and engineering, researchers strive to integrate data from optical microscopy (OM), scanning electronic microscopy (SEM), and transmission electronic microscopy (TEM). Currently, it is impossible to obtain a continuous image with high resolution in all domains.

To make the impossible possible, this project would develop the capability to simulate a large, high-resolution image based on a coarse image and several small, high-resolution images. The resulting image would help researchers identify the "hot spots," where complex chemical or mechanical phenomena are likely to be occurring. Further, we would develop the capability for researchers to simulate the performance and properties of complex heterogeneous materials. Drawing upon exascale computing, this new model would make it possible for multiphysics, multiscale simulation ranging from nanometer scale to meter scale.

We will develop the capability to integrate disparate data and create high-resolution images that cover large areas of a sample, providing a complete, detailed view of complex, heterogeneous structures with value to energy production, environmental remediation, and pharmaceutical innovation. We will integrate data from microscopes and other chemical imaging instruments that collect data based on specific physical, chemical, or topological properties. Usually, as the resolution of the chemical images increases, the area inspected decreases. With this project, we will build high-resolution images of large areas to understand fully a complicated biological or chemical phenomenon in a complex heterogeneous system. Further, our work will cross multiple scales, from millimeter to nanometer. We will achieve our goals through data reduction and merging resolutions.

In FY 2011, we started with a low-resolution, low-magnification OM image and multiple high-resolution, high-magnification SEM images to generate a large high-resolution image. A statistical correlation function was used in reconstruction. Source code was implemented and applied to chemical image integration of a dual-phase high-strength stainless steel sample. A strategy on using data reduction of statistical correlation function to expedite computation will be investigated. Also, information from low-resolution images will serve as input to reconstruct the high-resolution image.

We have begun image simulation on low-resolution image reconstruction using stochastic method. The experimental small area high resolution image a) and simulated large area low resolution image b) are illustrated below. We initiated the resolution merge study using different approaches, data reduction, and hue, saturation, and value (HSV) method. We used two images, a) and c), in the same area with different resolution as input. The fused image using HSV resolution merge is demonstrated in subplot d).



(a) Low resolution small area micrograph of dual phase stainless steel, (b) high resolution small area micrograph of dual phase stainless steel, (c) simulated large image with low resolution, (d) resolution merged image from image (a) and (b).

In FY2012, capabilities and tools will be developed to integrate the images from different areas but with same resolution into a large image with high resolution. Different resolution merge tools will be compared and optimized. High performance computing will be introduced in the integration algorithms to make it possible to generate large image at reasonable speed. We will work with research groups to apply our developed algorithms and tools for their application.

Material Interface Optimization in Extremely Thin Absorber Photovoltaics

Tiffany C. Kaspar, Timothy C. Droubay

◆ To meet the world's growing demand for energy, breakthrough technologies such as nanostructured photovoltaic (solar) cells are required. We investigated fundamental charge transport properties of relevant photovoltaic materials to aid in material selection and optimization. ◆

Nanostructured solar cell designs utilizing novel materials are necessary to realize a revolution in solar cell efficiency and cost. One such design is the all-solid extremely thin absorber (ETA) solar cell, consisting of a nanostructured *n*-type semiconductor (ZnO) coated with a thin layer of photon absorber material (CdTe) and impregnated with a *p*-type semiconductor (CuSCN). Others have shown solar conversion efficiencies of 2.3% for the ZnO/CdTe/CuSCN structure, but there is room for significant improvement. To achieve highly efficient charge separation and transport in ETA solar cells, the materials must be engineered such that the energy band alignments at the heterojunction interfaces are favorable for the desired charge transport (electrons into *n*-type ZnO and holes into *p*-type CuSCN). Despite the crucial importance of the resultant band alignments to the overall photovoltaic efficiency, heterojunction band alignments in solar cell materials are rarely measured directly. By directly measuring the band alignments with x-ray photoelectron spectroscopy (XPS), this fundamental study will open new paths to material selection, optimization, and solar cell design.

The thin-film heterojunction chosen for the first band alignment measurements in FY 2009 by XPS was ZnO on the *n*-type transparent top electrode $(In,Sn)_2O_3$ (ITO) because these oxides are easy to work with and the heterojunction is used in many technological applications. Pulsed laser deposition was used in FY 2010 to deposit various thicknesses of ZnO on ITO (1000Å)/quartz as well as thick ZnO and ITO reference standards. Thick films of 10% Sn-doped In_2O_3 (ITO, 100 nm) and thin films of ZnO were deposited on quartz by pulsed laser deposition (PLD) at 300°C in 10 mTorr O_2. For FY 2011, thin ZnO films were deposited in sequence on a CdTe(001) substrate, at 200°C in vacuum. Valence band and core level photoemission spectra were collected *ex situ* with a photoelectron spectrometer and monochromatic Al Kα x-rays, with an energy resolution better than 0.5 eV. DFT calculations were performed at the GGA, GGA+U and hybrid HSE06+U levels of theory for eight candidate interface structures;[2] results are given below only for the lowest-energy structure at the HSE06+U level.

Valence band offsets for ZnO/ITO heterojunctions were determined from the separation of shallow core level In 4*d* and Zn 3*d* peaks and comparison with core level-to-VB maximum measurements on material thick films. Valence band offsets for a series of ZnO films 12–40 Å thick is found to be in the range of -0.05 to -0.25 eV (ZnO VB maximum above ITO VB maximum). The CB offsets were calculated as -0.5 to -0.7 eV for ZnO films deposited on ITO/quartz. Some increase in surface oxidation of Te to Te^{4+} was observed after ZnO deposition. However, this surface oxidation will likely occur during photovoltaic device processing, and thus band offsets of this imperfect interface are of interest in real-world conditions. Core level analysis of the Zn $3p_{3/2}$ and Te^{2-} $4d_{5/2}$ peaks for 10 Å ZnO/CdTe places the valence band offset as +2.20 eV. The conduction band offsets determined for two ZnO thin film thicknesses are calculated to be 0.16–0.33 eV.

Hybrid DFT calculations (HSE06 + GGA) of epitaxial zinc blende ZnO on CdTe predict a valence band offset of +2.60 eV, resulting in a conduction band offset of 0.67 eV if the film is zinc blende (0.73 eV for wurtzite ZnO). These results are for the lowest-energy model interface with half-occupied (001) oxygen planes of zinc-blende ZnO bonding to Cd planes of CdTe, such that O atoms bridge between Cd atoms of adjacent chains on the (001) CdTe surface. For the same structure, GGA+U gave a band offset of 1.80 eV, while GGA gave only 1.05 eV. The Hubbard term with U=7.5 eV places the Zn 3*d* levels realistically below the ZnO upper valence band, preventing the VB maximum from being pushed up too high by *p*-*d* band repulsion. The hybrid functional corrects DFT underestimation of bulk band gaps, preventing spurious overlap of ZnO conduction with the CdTe valence band.

Type II band alignments are found for both ZnO/ITO and ZnO/CdTe; these band alignments should facilitate electron transfer from CdTe to ZnO to ITO, as desired for photovoltaic cells. However, the conduction band offset found for the ZnO/ITO interface is not ideal, since the large "cliff" in the offset will result in a significant amount of energy lost during electron transfer, which lowers the fill factor and open circuit voltage of the photovoltaic cell. In the case of CdTe/ZnO, the conduction band offsets are smaller, which is favorable for electron injection in a photovoltaic device. Interestingly, the measured conduction band offset (on heterojunctions with imperfect interfaces) is more favorable for efficient electron transfer than the predicted offset for the epitaxial system.

We met our goal to provide a fundamental scientific foundation to understand charge transport in novel oxide-based solar cells and tailor it by doping and/or interface modification of material systems. These results will provide the basis for improvements in solar cell efficiency in the quest to harness solar power to meet the world's energy demands.

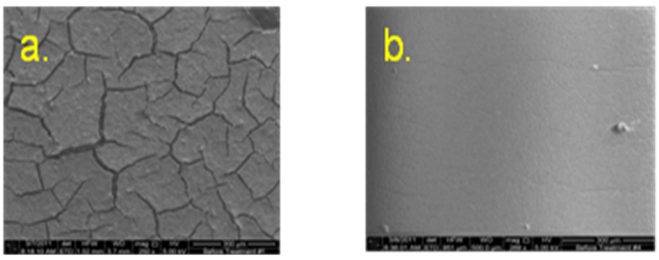
Materials and Methods for Low Cost Photovoltaic Manufacturing

John P. Lemmon, Qian Huang, Guosheng Li, Feng Chen

◆ Developing solution-based thin film photovoltaic (PV) manufacturing methods vs. the current costly high vacuum processes is significant to decreasing our nation's dependence on petroleum imports while reducing carbon emissions. ◆

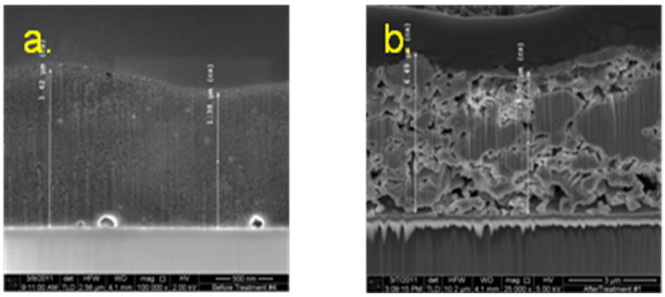
Currently, PV cells based on thin film copper-indium-gallium-selenide (CIGS) have emerged as one of the leading contenders for thin film solar technologies. Thin film solar cells utilizing CIGS as the absorber material have demonstrated over 19% efficiency in the small cell configuration, greater than 16% efficiency in production sub-modules and 11% in large scale production modules. However, despite offering great promise, the complicated nature of CIGS renders the deposition process quite complex and therefore time consuming and costly. An attractive approach to decreasing production cost has been the development of non-vacuum, solution based CIGS (and other low-cost absorbers) and is the focus of this project. The overall goal of this project requires new discoveries to meet aggressive performance targets, and the project is divided accordingly into phases and tasks, as below.

Develop metal nano-inks and deposition techniques. We previously reported a facile process to synthesize inks containing encapsulated metal nanoparticles of copper, indium, and gallium from low cost inorganic salts. A key challenge was establishing facile experimental parameters to reduce metal ions in solution to metal nanoparticles without forming metal oxides or particle agglomerates. To meet this requirement, we used a solution-based sodium borohydride reduction process that rapidly converted metal ions to their metal form. However, further workup of the inks into thin films for device fabrication proved to be limited by low vapor pressure. The uneven vaporization of the encapsulant caused micro-crack formation prior to the selenization reaction, which greatly affected the adhesion of the absorber film to the substrate after thermal processing. To mitigate cracking of the absorber film, we modified our nano-ink process using an extractable encapsulant that allowed for the use of a high vapor pressure solvent that evaporates evenly during thin-film deposition. A high vapor pressure solvent also allowed for spray deposition that produced uniform films within the tolerance of 0.5 µ.



a) CIG film deposited using nano-inks developed in FY 2010 show micro-cracks; b) CIG film spray deposited using new encapsulant for FY 2011.

Optimize CIGS films. Pervious results from FY 2010 showed that nano-ink deposited films could lead to single phase absorber materials with the desired composition. The microstructure of the films was also optimized by using a design of experiments approach during the selenization reaction and subsequent thermal annealing process. However, micro-cracks formed during ink deposition led to poor film adhesion and subsequent delamination upon additional cell work up. Recent processing improvements in film deposition and selenization accomplished last year led to dense absorber films amenable to more PV cell workup. The results stacked nanoparticles deposited using a spraying technique and further reacted to form large grain absorber crystallites necessary for high efficiency PV performance.



a) SEM cross section of a spray deposited CIG film showing stacked nanoparticles; b) SEM cross section of converted CIGS film showing large grain growth.

Fabricate small-scale superstructure CIGS photovoltaic cell. Significant progress was made in FY 2011 toward the fabrication and performance evaluation of full PV cells generated from materials in Phase I. This included the development of several thin film layers required for PV cell operation, including CdS window and TCO-HRT layers as well as full cell fabrication and performance test results. Although the measured efficiency is below the target goals for the project, these result represent our first attempts to produce full PV cells. The low efficiency can in part be explained by the low photo-current generated by the PV devices. These results indicate that recombination of charge carries coupled with high film resistivity are major contributors to the low performance in these cells. The program is now focused on further optimization of the thin film processing to yield higher efficiencies and develop large format cells for FY 2012.

Our project has produced new PNNL capabilities. We developed an in-situ optical reactor that utilizes sapphire window for monitoring chemical reactions and processes with a 3–5 μm thermal imaging camera. It can monitor real temperature changes from free energy differences in chemical reactions or emissivity changes in reaction surfaces that correlated to the formation of new products. The project will move into Phase II for FY 2012, where CIGS microstructure will be further optimized and performance tested in PV cells to determine overall efficiencies and impact on cost.

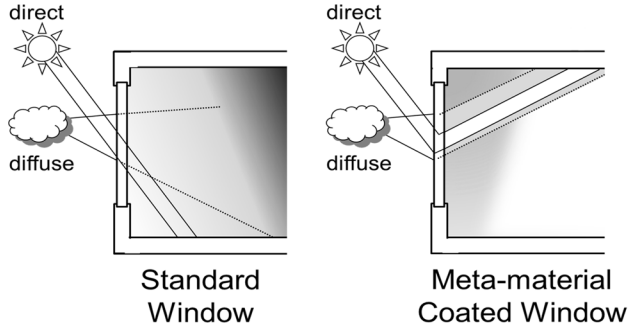
Meta-Material Coatings for Daylighting Windows

Kyle J. Alvine, Bruce E. Bernacki, Albert Mendoza, Dean W. Matson, Wendy D. Bennett

◆ The goal of this project is to develop advanced windows coatings to bring daylight significantly further into buildings to offset the usage of artificial lighting. If successful, this new coating technology is projected to save up to 0.66 quadrillion BTUs of energy and offset nearly 12 million tons of carbon per year over standard windows. ◆

The ability to tailor the redirection of light through innovative low-cost nanostructured meta-material coatings would revolutionize energy consumption for building lighting and energy production using solar technology. Interior lighting currently accounts for the largest portion of electricity consumption in the commercial building sector at about 3.5 quads. Standard daylighting schemes with penetration of 15 feet have potential to save 1 quad of energy. The ability to redirect light even further into a building to 30 feet with nanostructured coatings should lead to a near doubling the energy savings from standard daylighting. This would be a game-changer for building energy usage.

The objectives of this project were to develop the necessary nano-fabrication and numerical modeling tools to produce meta-material based advanced windows coatings that can redirect light significantly deeper into a building. In addition, we also fabricated and characterized preliminary coating samples partially to test proof-of-principle.



Schematic comparison of daylighting from a standard window (left) to a meta-material coated window (right).

During FY 2011, we have developed nano-fabrication tools and expertise along with numerical modeling tools to produce meta-material windows coatings for light redirection. We developed numerical modeling tools based on Maxwell's equations to predict the optical response of meta-material coatings for windows. Specifically, we have focused on the wavelength response and light redirection from meta-material coatings that we designed. For these meta-material coatings, the angle of light redirection upon transmission is set by the meta-material internal structure and can be varied as required. The response was quantified in terms of variables that could be controlled through design and fabrication, such as structure thickness, length scale, material composition, and shape. Wavelength response was also quantified between 400 nm and 1100 nm to cover the entire visible light spectrum and to gather partial information about infrared and ultraviolet response as well.

Based on our numerical modeling results, we used a combination of nano-lithography and metal sputter deposition to fabricate preliminary meta-material coatings on glass. Samples were on the order of ½"× ½" and highly transparent. In FY 2011, we focused our efforts on single wavelength response structures. Concurrently, however, we developed designs to produce multi-wavelength response. To quantify the optical response of these preliminary samples, we constructed a variable-wavelength test rig. The rig can scan the incident wavelength from 400 nm (blue end of the spectrum) up to 1100 nm (red end of the spectrum). This range incorporates all of the visible light spectrum and can also yield information about a portion of the infrared and ultraviolet response of the meta-material. Light scattering and transmission from the sample was measured with a combination of an area detector and a more sensitive photo-diode mounted on a goniometer to quantify angular response.

Our optical measurements on the preliminary samples showed a pronounced transmission resonance response in the wavelength near 650 nm (~ red light) as expected from our design. This is confirmation that our coating has a meta-material type response. The resonance was pronounced, but fairly broad in wavelength which is highly beneficial for the next phase of producing a multi-wavelength response. In addition we observed light redirection at the resonance wavelength from the structures. From these preliminary samples, the ratio of the redirected light to the incident light is only a few percent. However, we expect that this can be substantially improved through changes in both the meta-material structure design and the nano-fabrication to approximate our designs more closely.

We identified that the two main technical challenges facing this daylighting windows technology are (a) converting from single wavelength to the full visible light spectrum and (b) improving the ratio of redirected light to transmitted light. While both aspects are essential, we will focus our FY 2012 efforts on modeling, fabricating, and quantifying coatings that demonstrate light redirection over the full visible light spectrum.

Multiphysics Capability Development and Application to Magnesium Alloys

Erin I. Barker, Ramaswami Devanathan, Dongsheng Li

◆ The primary aim of this project is to develop and demonstrate multiphysics material models relevant to energy technologies, especially in advanced nuclear energy systems and lightweight alloys for transportation. ◆

Multiscale, multiphysics models are widely applicable to material science problems. There is growing interest in developing lightweight alloys for transportation technologies; for example, DOE has set an automotive target of 50% weight reduction relative to steel without loss of performance. While one could replace the body panels of cars with expensive lightweight alloys, the weight savings cannot be justified by the higher cost. The most promising area for improving vehicle efficiency through lightweight alloy substitution is in the engine because of its weight. Lightweight magnesium (Mg) alloys are promising but would require the addition of rare-earth elements. Because obtaining this material depends on suppliers in sensitive foreign markets, it is desirable to develop Mg alloy compositions that have appropriate temperature characteristics without the use of the elements.

Traditionally, alloy development has followed a heat-and-beat approach that is expensive and cumbersome. However, we will strive to combine information from multiphysics simulations, data from literature, and experimental results to develop rules that can guide alloy selection and create a new capability. This would include building synthetic microstructures for computational analysis, developing material models appropriate at the microstructure scale, and demonstrating multiscale material modeling. Development of this method would add value to material modeling efforts, create a much-needed capabilityat PNNL in the area of materials research.

Previously, we surveyed the available interatomic potentials for Mg alloys and chose a potential for our simulations. Based on the modified embedded atom method, the potential provides a satisfactory description of point defect and thermo-mechanical properties as well as Mg-Al alloy behavior. At the microstructure scale, we developed a preliminary algorithm for generating 2D realizations based on Mg alloy microstructures. A parametric study of sensitivity to material parameters for elastic-vosciplastic material model describing Mg alloys grains began using 3D generic microstructure representations.

During FY 2011, we expanded automated software capabilities for generating 3D and meshing synthetic microstructures containing different microstructural features of interest in Mg alloys that can be utilized for finite element analysis. While reconstructing digital representations of experimentally observed microstructures can be useful for validating simulation results and material models against a single test, it is a time-consuming, self-limiting technique. Rather than attempt to reproduce results from a limited set of experiments, we are supplementing the physical with digital experimentation. By extracting statistical information about microstructural features (such as bulk porosity, average pore and grain size, and orientation distribution) and creating a suite of synthetic microstructure samples, we can conduct parameter and sensitivity studies to isolate how individual features influence material response and how variation in these features improves or reduces response.

Given average grain size or number of grains and an orientation distribution, statistically equivalent 2D or 3D polycrystal samples are being generated. The insertion of sub-grain sized pores or inclusions was added this year. Pores or inclusions are represented as ellipsoids and randomly placed within the grains. The ratio of the axes can be held constant or varied from pore to pore. The influence of porosity on the ductility of cast Mg, where a defined grain structure is not present is also an area of interest. Therefore, the insertion of pores has also been applied to single material samples. Also, finite element meshes are generated for analysis of the samples. A requirement of meshing is that internal boundaries (such as grain and pore/inclusion-grain interface) be respected, allowing for the insertion of interface elements for modeling decohesion and sliding. Inclusions and pores are represented the same geometrically as ellipsoids. During the analysis, pores are represented as voids in the mesh; therefore, the algorithm was modified to alloy for the ellipsoids either to be meshed and assigned a material ID or the mesh removed, leaving a void.

In FY 2012, we will continue improving the insertion of pores/inclusions in polycrystal samples. We will extend placement to allow pores/inclusion to be inserted along grain boundaries. Analyses will also be expanded to incorporate the use of cohesive zone models along grain boundaries and grain-particle interfaces to model decohesion and crack initiation as a failure mechanism within the samples. A new cohesive zone model will be developed to include degradation due to the presence of corrosive elements and the propagation of the corrosion along the grain boundaries. Scaling studies of the current finite element analysis framework will also be conducted. Further, identifying and improving software and algorithmic bottlenecks will help increase the number of analyses that can be conducted and allow us to continue to increase the fidelity of our models.

Multiscale Charge and Ion Transport Simulations for Nanostructured Electrodes

Kevin M. Rosso, Maria L. Sushko, Shenyang Hu, Yulan Li, Peter V. Sushko

◆ This project will develop and perform first ever simulations of collective charge transport dynamics from the atomic to micron scales for coupled electron and ion transport in polycrystalline metal oxide electrodes. A deep, fundamental understanding of the basis for electron and ion conductivity would guide the synthesis of novel electrode materials with significantly enhanced performance. ◆

Titania (TiO_2) is an attractive alternative for carbon-based cathode materials in lithium ion batteries because of its high surface area, chemical stability, and high theoretical capacity. Several polymorphs of TiO_2 have been shown to benefit significantly from nanostructuring or from the incorporation of nanoporosity. Increased rate capability, capacity, and tolerance for strain from lithium insertion/extraction have all been reported for TiO_2 nanomaterials. Although nanostructuring and nanoporosity offer improved performance because of higher contact areas between electrolyte-electrode and shorter diffusion distances for lithium ions and electrons, there is a lack of fundamental understanding about the effects on coupled electron and ion transport efficiency of nanosizing electrolyte-electrode interfaces and of the interdependence of electrode materials and electrolytes, contact areas, and diffusion distances, thus preventing reliable predictions of performance.

As a result of the issues raised above, a long-term goal of our research is the discovery of design principles for nanostructured metal oxide electrodes that maximize ion and electron diffusivity. The first step in this process is to improve our understanding of charge transport in electrode materials such as the TiO_2 polymorphs. In particular, the fundamental understanding of the effect of electrode nanostructuring and the physics of charge transport at the nanoscale, which includes the elucidation of the role of defects and grain boundaries, has to be developed.

Our FY 2009 activities focused on performing molecular dynamics simulations of the kinetics of coupled electron and lithium ion transport in $LiTiO_2$ polymorphs for comparisons with experiments and also to examine fundamental processes that potentially impact anode performance in lithium batteries. We concentrated on the two most stable and most studied TiO_2 polymorphs: rutile and anatase. Also, molecular dynamics simulations were performed with a potential shell model to investigate the diffusion of Li^+ and electron polarons in rutile and anatase. In all, the project met or exceeded its fiscal year milestones. Multiscale simulations of Li^+/electron transport in TiO_2 nanoparticles led to the publication of one manuscript and submission of another in high quality journals. Density functional theory simulation of coupled Li^+/electron transport in olivine phosphates and the embedded cluster simulations of Li^+ in reduced TiO_2 both led to the submission and publication, respectively, of one manuscript each to a high-quality journal.

In FY 2010, this project focused on elucidating the mechanism of coupled electron and Li^+ transport in TiO_2 nanoparticles to predict the size, crystal structure and orientation of TiO_2 nanoparticles, which would enhance the performance of nanostructured cathode materials for Li batteries. We also continued the investigation of elementary Li^+/electron transport in bulk materials and in the vicinity of defects. To achieve these goals, we developed novel software for multiscale simulations of one-dimensional charge transport and equilibrium properties of multicomponent systems and used it to study the mechanism of charge transport in TiO_2 nanoparticles. Finally, we developed quantum mechanical embedded cluster model for simulation of elementary Li^+/electron transport in the vicinity of defects and grain boundaries.

The results on the elementary Li^+/e^- transport in TiO_2 polymorphs obtained in FY 2009 were used in FY 2010 to simulate charge transport on the nanoparticle level. In particular, diffusion barriers for Li^+ and electron polaron elementary transport in bulk materials were used to parameterize the kinetic Monte Carlo and Poisson-Nernst-Planck models. Kinetic Monte Carlo simulations were used to study the influence of explicit Li^+/e^- coupling, interfacial contact area with the carbon matrix, and charge injection flux and grain size on Li^+/e^- conductivity in TiO_2 nanoparticles. These simulations revealed that charge diffusion rate increases with the increase in injection flux and with the decrease in the grain sizes.

To elucidate the fundamental mechanism for the dramatic increase in Li^+ conductivity with the decrease in the size of the nanoparticles, we employed the Poisson-Nernst-Planck method. Using this approach, we showed that the competition between Li^+ and electron accumulation at the nanoparticle boundaries competes with the steady ion and electron fluxes. For nanoparticles smaller than a critical size (equal to 20 nm for rutile and 5.7 nm for anatase), the balance is shifted towards the steady charge transport (hence high conductivity), while for larger nanoparticles, charge separation prevails. Size effects are also manifested in the change in the nature of charge transport from dual ionic/electronic for small nanoparticles to predominately ionic for larger ones. Simulations revealed that the temperature dependence of Li^+ conductivity in anatase is very weak, while in rutile the

conductivity decreases with temperature in small nanoparticles and increases in large nanoparticles. These results generated two papers in high quality journals.

We studied the effect of oxygen vacancies on Li^+ diffusion in rutile TiO_2 using the embedded cluster approach. We found that the calculated Li^+ diffusion pathway in vacancy-containing lattice is similar to that found for the ideal lattice. However, vacancies strongly modify the shape of the Li^+ potential energy surface and increase the diffusion activation energies by the factor of two. Based on these results, we published a paper in a high quality journal.

In FY 2011, we built on the simulations from the previous two years to develop a general hierarchical multiscale modeling approach of charge transport in nanostructured electrode materials and to study more realistic systems, which have defects and grain boundaries.

On the methodological side, we have developed novel hierarchical hybrid multiscale simulation technique for modeling coupled ion and electron transport in nanostructured energy storage materials. The model uses multiphysics approach, in which instead of formal consecutive upscaling we introduce novel types of collective long-range interactions along with short-range effects of the finer scale models. The fine scale model take advantage of high accuracy embedded cluster quantum mechanical simulations of elementary charge transport as well as the state-of-the-art molecular dynamics free energy simulations of coupled ion and electron diffusion. The collective long-range electrostatic and excluded volume interactions are introduced on the mesoscale (10–300 nm) via classical Density Functional theory coupled with Poisson-Nernst-Planck formalism for dynamic effects. The mesoscopic free energy, which includes contribution from short-range activation dynamics of ions and electrons, derived in the atomistic models, is then used in a larger scale (microns) phase field model to simulate charge transport in a network of nano-sized grains. As a demonstration of the application of the model for elucidating the basic principles of charge transport in nanostructured energy materials, the fundamental physics of Li^+ and electron transport in nanostructured TiO_2 was studied.

Using this multiscale model, we have shown that charge distribution and electric potential in the network of TiO_2 naoparticles depends on their mutual orientation. The increase in the angle between c-axes of the nanoparticles leads to higher anisotropy in electric potential in the system and to more significant charge accumulation at the nanoparticles boundaries. These data provide the guide for designing electrode microstructure for enhanced power output during the charge/discharge processes.

To address the problem of charge transport in more complicated materials with highly nonlinear ion transport pathways, we extended our one-dimensional Poisson-Nernst-Plank/classical Density Functional theory model to three dimensions. Using this improved model we have performed simulations of Li^+ and electron conductivity in lithium phosphorus oxynitride, one of the most widely used solid electrolytes. By comparing the results of one- and three-dimensional models, we show that for this material with complex non-linear Li^+ diffusion pathways, three-dimensional description is essential for reproducing experimentally measured conductivity. We have shown that the conductivity in this material strongly depends on temperature and on the size of nanoparticles/film thickness. The increase in conductivity at lower temperatures was found to be due to the increase in electrostatic correlation interactions between Li^+, which promotes the directed flow of ions through the material. The size of the nanoparticles/film thickness determines the effective concentration of Li ions available for the constant flow in this material. In particular, lithium phosphorus oxynitride film with a thickness smaller than 10 nm would provide the highest conductivity. These findings can guide the design of solid electrolyte films for low and high temperature battery applications. The study was submitted to a high quality journal.

Our recent work on the development of the embedded cluster approach was focused on the first ever simulation of electron-polaron transport in stochiometric rutile and in rutile with oxygen vacancy using high quality quantum chemistry methods, such as Moller-Plesset second order perturbation theory. The results reveal a crucial role of full account of electron correlation and exchange interactions, which are only partially present in standard density functional approaches.

Photocathode Development for Next-Generation Light Sources

Wayne P. Hess, Theva Thevuthasan, Scott A. Chambers

◆ This project will develop robust photocathode sources with intense electron yields and ultralow thermal emittance. We expect to design several new photocathode sources using inventive semiconductor, mixed-metal, and composite designs. Our ultimate goal is to produce versatile new photocathode designs to enable construction of fourth generation light sources at significantly reduced cost. ◆

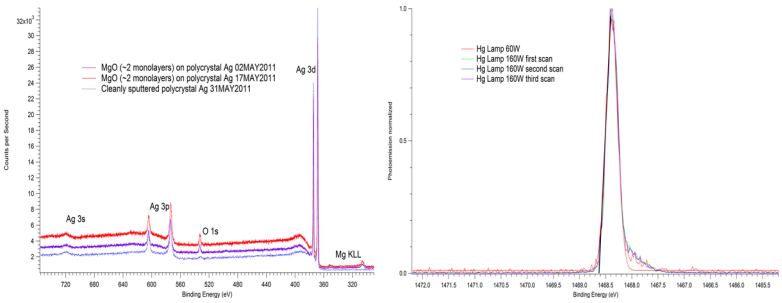
Photocathode technology must be advanced to meet the needs of fourth-generation light sources. Whether based on free electron laser (FEL) or storage ring designs, the ultimate output characteristics and cost of next-generation ultraviolet (UV) or x-ray sources are heavily dependent upon photocathode brightness and emittance characteristics. Novel photocathode designs could potentially reduce light source construction costs dramatically by significantly simplifying downstream accelerator or FEL design. The international light source community recognizes the need for a more scientific approach to new photocathode development and is in the initial stages of addressing this issue. The fields of materials science, solid-state photochemistry, and surface science can and should make an immediate and timely contribution to this essential activity.

We aim to create new photocathode materials and designs to make fourth-generation light sources a reality. We will develop robust photocathode sources with intense electron yields and ultralow thermal emittance. Our ultimate goal is to produce versatile new photocathode designs to enable construction of fourth generation light sources at significantly reduced cost. Specifically, we will directly address photocathode durability by understanding the mechanisms of photocathode degradation. The project will first develop innovative photocathode materials and designs, such as quantum-well structures, vertical pillar nanostructures, and cluster-based nano-composites, using novel semiconductor, mixed-metal, and wide-bandgap materials coated on metals; and second, demonstrate high electron bunch intensity, low thermal emittance, and operational durability required by next-generation light sources.

During FY 2011, we completed construction of a multi-source thin film deposition chamber, including installation and testing of three effusive ovens for chemical vapor deposition and vacuum sample transfer. We interfaced laser (3.8 eV helium cadmium) and UV (broadband mercury) lamp excitation sources and installed non-evaporative getter pump to reduce base pressures of the XPS instrument into the 10-10 torr range. We tested the deposition chamber by coating a polycrystalline silver substrate with two monolayers of MgO and performed XPS and UPS on the hybrid sample. Next, we further modified the photoelectron spectrometer to characterize photocathode properties, including photon energy dependent electron yield (bunch intensity) and emittance (electron angular distribution). A hybrid photocathode was created by coating a polycrystalline silver substrate with two monolayers of MgO. We then conducted XPS and UPS on the hybrid sample. Our initial in situ growth of coated photocathodes and interrogation by UPS and XPS angle resolved photoemission spectroscopy constituted a project milestone.

In late FY 2011, we tested the hypothesis that the metal substrate could reduce the sensitivity of MgO to photo-degradation by UV light. The thin MgO layer on silver was indeed stable under UV irradiation. No loss of XPS signal is observed after 24 hours of UV irradiation. A filtered mercury lamp (< 4.1 eV) was used to measure the work function of the hybrid system. The electron analyzer assumes an aluminum anode x-ray source (1486.69 eV). We use a linear extrapolated leading edge and a –15 V sample bias, yielding a 3.05 eV work function of MgO:Ag. The work function of polycrystalline Ag is 4.26 eV. The UPS results confirmed the predicted reduction in work function from 4.3 to 3.0 eV.

For FY 2012, we will initiate ab initio modeling of Cu:KBr (and possibly Ag:MgO) thin film structures and electronic properties and will compare the results to photocathode emission studies to test predictions of enhanced bunch intensity. Using angle-resolved UPS, we will measure thermal emittance to demonstrate the utility of hybrid materials. We will use photoemission electron microscopy to show that novel nanostructured photocathode designs display enhanced yield (bunch intensity) compared with polished metal photocathode. Finally, we will use modeling and photoemission measurements to determine the role of intraband defects in metal supported alkali halide and metal supported MgO systems.



Two monolayers of MgO on a polycrystalline silver substrate were interrogated by x-ray photoelectron spectroscopy (XPS; left panel) and UV photoelectron spectroscopy (UPS; right).

Rare Earth-less Permanent Magnet

Jun Cui, Glenn J. Grant, Curt A. Lavender, Carlos A. Fernandez, John S. McCloy, Wendy D. Bennett

◆ We propose to develop a new strong magnet material containing zero rare earth (RE) elements to benefit the United States in both energy security and technology leadership. ◆

Unlike batteries, the energy of a magnet is not drained away and is always available for use. Because it does no "network" on its surroundings, a magnet lends its energy to assist the conversion between electrical and mechanical energy. Efficiency of the energy conversion is directly proportional to the strength of the magnet. Currently, all known strong magnets contain light rare earth elements and transition metals. This requirement is attributed to the exchange coupling between the rare earth and transition metals moment, which results in generally larger magnetic moments for intermetallics of light rare earth and transition metals. However, there exists a shortage of rare earth elements, in part due to their being a large component in hybrid electrical vehicles. Thus, there is a growing desire to develop alternative magnetic materials based on domestic ore reserves to mitigate reliance on foreign sources.

The current state-of-the-art permanent magnet is $Fe_{14}Nd_2B$. Its maximum energy product, $(BH)_{max}$, has reached 60 MGOe in a lab demonstration. The key to its high $(BH)_{max}$ is the exchange coupling between its hard phase ($Fe_{14}Nd_2B$) and its soft phase (Fe_3B). The term "hard" or "soft" refers to the difficulty to magnetize the materials or the magnitude of the coercivity field, H_c, where high H_c means hard and low H_c is soft. Based on this principle, we propose to create a nano-composite with MnBi as the hard phase and Fe as soft. The maximum energy product of the resulted MnBi-Fe is about 50% of the $Fe_{14}Nd_2B$ at room temperature. Unlike most ferromagnetic materials whose H_c decreases with increasing temperature, the H_c of MnBi rises with increasing temperature and reaches maximum at ~300°C. This feature is particularly striking compared with the $Fe_{14}Nd_2B$ magnet, whose H_c rapidly deteriorated when temperature is >80°C.

Four critical tasks were carried out in FY 2011: 1) thin film exploration of exchange coupling between MnBi and Fe, 2) stir friction consolidation of the NdFeB/Fe composite, 3) solution-based nano synthesis of MnBi and MnBi/Fe core/shell particles, and 4) theoretical analysis of the MnBi/Fe nano composite configuration, processing, and performance. Our efforts focused on developing novel magnet fabrication techniques such as nanosynthesis, air atomization, melt-spining, and stir-friction.

Both magnetron sputtering and ebeam deposition were used to prepare MnBi/Fe multilayer thin films. Obtained films were heat-treated in a protected environment at 220~400°C for 2~10 hrs. EDS was used to analyze the composition, x-ray diffraction was used to analyze the phases, and VSM was used to characterize the film magnetic behavior. To date, necessary evidence showing coupling between MnBi and Fe has been obtained. The composite film shows increased magnetization by adding Fe layer, while slightly loss of the coercivity with kink-less MH curve was observed. However, the overall coercivity is about 700 Oe, which is one order of magnitude less than the reported value. We contributed this behavior to poor film quality. The team is currently working on adjusting the film's composition to maximize the ratio of the magnetic phase, as large coercivity is critical for a high performance permanent magnet.

Also during the last fiscal year, MnBi nanoparticles were successfully synthesized using solution based method. Several approaches with various combinations of solvents, reducing agents, and stabilizers were explored. We found that employing 1-methyl-2-pyrrolidone instead of oleyamine as solvent afforded nanocrystal formation with a good yield, small size (a few nm), fairly low size distribution, and a spherical shape. This approach has been scaled up to 1g. The ability to synthesize MnBi nanoparticles with accurate composition, size, and shape is critical for an economical production of the MnBi-based magnet in large quantity.

Stir friction consolidation offered high-density packing with minimum grain growth, which is particularly suitable for magnet fabrication. However, stir friction requires large capital for equipment. Our first puck was produced after 9 months of preparation. Several iterations minimized oxidization and optimized the heat dissipation. The obtained samples are currently being characterized using SEM, XRAY, and VSM.

Theoretical analysis of the MnBi/Fe composite configuration and entitlement based on Skmoski model were carried out, showing maximum energy of 30 MGOe at room temperature and 52 MGOe at 200°C. This finding is exciting because the most strategically critical rare earth element, Dy, is used in the NdFeB-based magnet to sustain high temperature performance. If we could realize MnBi/Fe's high temperature properties predicted by the model, we should be able to address the Dy shortage issue effectively.

In FY 2012, we will improve the MnBi-Fe nano-composite magnet concept and develop a prototype magnet. We will also continue with each of the four tasks but focus more on processing, a critical step for scale-up.

Site Specific Atomic Resolution Probing of Structure-Property Relationship Under Dynamic and/or Operando Conditions Using In Situ and Ex Situ Chemical Imaging Based on Multi-Instrument Approach

Chongmin Wang, Libor Kovarik, Satyanarayana V.N.T. Kuchibhatla

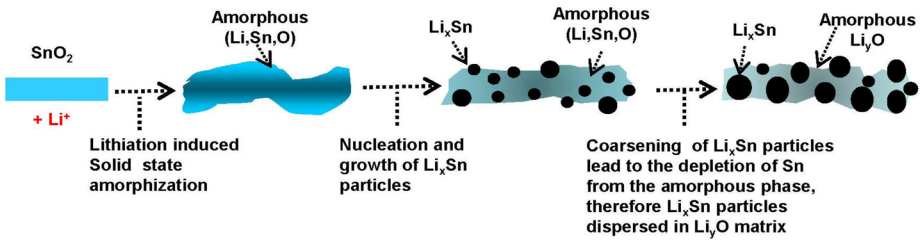
◆ This project aims to develop in-situ capabilities for chemical imaging that will lead to the advances and discovery of new materials for the energy security and efficiency. ◆

Energy and environment are key issues challenging mankind and are central to DOE. Many fundamental scientific problems related to these issues involve the control of chemical and biological processes. Advancement in scientific innovations is often driven by precise, atomic-level characterization of materials of interest as this, in turn, renders the ability to precisely control/manipulate the material properties. However, existing tools and capabilities to measure the molecular details of chemical and biological reactive site structure and function limit our understanding and ability to control natural and human-made systems. The key to enhancing an understanding of the above energy/environment materials is to capture and visualize the atomic-level mechanisms under dynamic operating conditions, such as the structural evolution of the active materials in a battery during its operation, a catalytic process during the functioning of the system. Although the atomic-level structural and spectroscopic information under high vacuum conditions have been developed to a stage that can be routinely used (such aberration-corrected scanning transmission electron microscopy/transmission electron microscopy [S/TEM], atom probe tomography [APT], and atomic force microscopy/scanning tunneling microscopy [AFM/STM]), atomic-level imaging and spectroscopic analysis under dynamic operating conditions remains to be established. It is thus critical to develop tools and capabilities that enable atomic-level in situ measurements of complex systems under dynamic operating conditions, particularly at the same site while across different platforms of instrumentations, thereby providing complementary information.

The goal of this project is to develop chemical imaging capabilities that drive the atomic-level imaging and spectroscopic analysis of materials related to energy and environmental issues under in situ/operando condition and lead to the development of much-needed materials for next-generation energy and environment-related applications. This will be achieved by extending the state-of-the-art aberration-corrected S/TEM and other complementary microscopy and spectroscopic imaging capabilities to a new level, enabling atomic-resolution imaging and spectroscopic analysis under dynamic operating conditions. Further, new capabilities will be developed to enable complementary integration of site-specific atomic resolution structural and chemical information obtained from various techniques, including STEM/TEM, APT, and focused ion beam and scanning electron microscopy (FIB/SEM).

We made several key accomplishments in FY 2011 for advancing chemical imaging capabilities in PNNL and using these capabilities probed into the fundamental scientific challenges related to energy and environment. Our work was carried out from three aspects: energy storage materials, catalysis, and integration of capabilities across different platform. At first, we developed aberration-corrected S/TEM with proven Angstrom resolution for STEM imaging and sub-Angstrom information limit for HRTEM imaging. We demonstrated semi quantitatively the importance of the environmental effect on the spatial resolution of high sensitive instrument using S/TEM as a specific example. We mitigated the environmental effect on the imaging resolution of S/TEM, therefore enabling the imaging of catalyst particles with atomic spatial resolution and single atom sensitivity. Further, we developed the capability that allows nanoscale manipulation and biasing of sample in a transmission electron microscope. This capability allows us to image the materials while applying an external stimulus, which will play a key role for in-situ TEM research on battery and therefore allow us to probe into the challenge that facing the lithium ion battery community as why a lithium battery failure following the cyclic charging and discharging.

To observe the catalytic action of a catalyst during the operation, we developed the heating stage based on micro-electro-mechanical system (MEMS) technology for the aberration corrected S/TEM. This capability enables controlled rate heating of sample at a



Schematic drawing showing the proposed model for the structural evolution of SnO_2 upon initial charging.

localized area, which allows us to probe into the questions such as deactivation mechanism of catalytic properties. At the same time, we also developed a capability that enables imaging of a sample across the platform of FIB, APT, and STEM. This capability is the key for imaging a specified site of a sample across different instrument platform, yielding complementary information. Those new capabilities enable us to probe energy materials under the reaction conditions and capture complementary information across different instrument platform. The fundamental in-situ concept and capabilities developed in this project have great impact on the research community related to energy materials. The in-situ concept we developed has been implanted and used by other national laboratories and universities across the globe and the result advances the field on in-situ studies of energy materials.

With the new capabilities, we probed into the following scientific questions. For energy storage, SnO_2 is a representative anode material for lithium ion battery. Based on our in situ work, we proposed a model for structural evolution of SnO_2 anode upon initial charging. This work provides deep level knowledge as how the structure of the anode materials evolves during the first operation of the lithium ion battery. For the catalysis research, we derived morphological models of sub-nanometer Ir nano-clusters and the way they are epitaxially related to the spinel oxide substrate. The models are currently being refined with ab-initio calculations => identification of the $MgAl_2O_4$ terminating plane and the nature of the bonding across the interface. Based on STEM image simulation, we determined the limitations of "single-shot" STEM HAADF imaging for a direct determination of three dimensional atomic crystalline clusters. For the Au nano-clusters embedded in MgO, we carried out HRSTEM, EDX mapping, and APT analysis on similar tips. We noticed that the dimensions of Au-nanoclusters embedded in MgO in all the three cases agree very well. Highly coherent, sharp-interface was observed between the Au-nanoparticle and MgO. We found that the nanoparticles are composed of Au, Mg, and O as evidenced by the APT data. These results will be further confirmed by theoretical studies to estimate thermodynamic stability of Au-MgO intermixing.

Looking toward FY 2012, we will continue our effort on integrating image and spectroscopy methods using electrons, photons, and ions and ab initio modeling toward developing a physical-based understanding of catalytic phenomena. Specifically, we have the following capabilities in mind for the subsequent effort. We will integrate the results obtained using in situ TEM and x-ray absorption (such as integration of in situ TEM and STEM with STXM). In this effort, we have visited Canadian Light Source and developed a collaborative research plan under the general guidance of user proposal process. In the meantime, we will establish capability that enables in situ gas flow experiment in aberration corrected ETEM. This capability will extend our capability for chemical imaging at an environment up to the atmospheric pressure and temperature of up to 1200°C. We will use these in situ capabilities to probe anode and cathode materials to establish the failure mechanism of battery. For the catalytic materials, we will probe the atomic level structure and properties relationship to guide design of new catalyst. At the same time, great effort will be made to integrate in situ observation with multiscale predictive modeling to accelerate new energy materials discovery. Continued effort will also be made to integrate TEM and APT imaging for energy materials.

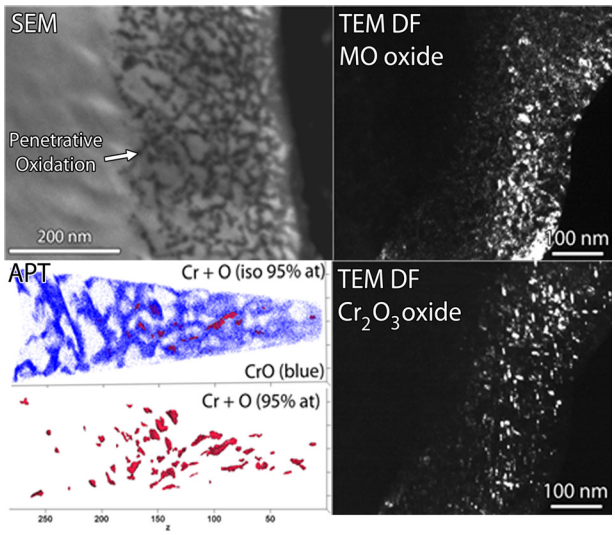
These continued efforts will duly serve the objective of our proposed research that aims to develop new research capabilities for probing into the dynamic structure-property relationship of materials relevant to energy security, such as energy storage materials and catalysts. The complementary use of these imaging, spectroscopic, and diffraction tools will allow extraction of information at the highest possible resolution about the atomic structure, electronic structure, coordination chemical environment, and spatial distribution. This atomic-level structural information will be coupled with the materials properties, such as catalytic properties, ion and charge transport in energy materials, and deactivation mechanisms of active materials for energy storage. We believe this research will significantly improve our current understanding of the functionality of materials under operando environments in energy storage and catalytic applications and will guide the design of next-generation materials.

Surface Damage and Environment-Induced Cracking Precursors in Light Water Reactor Components

Matthew J. Olszta, Danny J. Edwards, Mychailo B. Toloczko, Bruce W. Arey, Stephen M. Bruemmer

◆ Unique insights into the influence of surface preparation and reactor aging will be obtained for the first time, which will define relevant precursor states. The fundamental understanding of near-surface microstructures as a function of key service parameters will lead to improved predictive methodologies for crack initiation and significant advances in the non-destructive detection of crack precursors. ◆

A paramount issue impacting the performance, safety, and life extension of current light water reactors is the environment-induced cracking of structural components. Nuclear regulatory and industry groups worldwide have identified specific concerns within materials degradation management programs. Considerable work is still needed to be able to model long-term performance effectively and to secure the reliability of critical components. The stress data is used to understand stress states and water conditions that the components may have experienced during their lifetime and how crack propagation occurred. The results of this project will enable a better understanding of surface structure and morphology in light water reactor components exposed to practical surface treatments and service environments.



Exposure of high Cr, Ni base alloy surfaces under PWR water conditions illustrates a unique penetrative oxidation mechanism that appears to contradiction the conventional notion that a continuous, protective oxide is formed. The structure and chemistry of this oxidation mechanism was elucidated through complimentary SEM, TEM, and three-dimensional atom probe (APT) analysis.

State-of-the-art, multiscale investigations of the restructured surface will provide quantitative insights into the depth, extent, and microcharacteristics of near surface damage layers. Detailed knowledge of deformation microstructures will improve understanding of time dependent corrosion/oxidation processes and stress corrosion crack initiation pathways. Exposure to light water reactor environments at high temperatures will help elucidate the development of precursor states in restructured near surface morphologies leading to crack initiation and propagation. Using site-specific sample preparation techniques allowed by focused ion beam milling, the entire surface and near surface regions can be prepared and analyzed as one continuous uniformly electron transparent sample. The preparation and analysis will allow for a complete picture of surface structures and precursor crack initiation sites in light water reactor components.

In FY 2010, we prepared samples with ground surface microstructures and arranged them in a reverse u-bend geometry under constant loading, and exposed the samples. Unfortunately, the timeframe for these exposures was not enough to initiate cracking; hence, the direction of research shifted. During FY 2009, the experimental setup for these experiments was derived, and exposure did not begin until mid to late FY 2010. As with any SCC exposure experiment, it is necessary to hold samples for longer periods to time to induce cracking. Later experiments would hold these types of samples for longer periods to induce crack initiation.

During FY 2011, it was determined that experimental reverse U-bend samples created and exposed to PWR water conditions did not have the proper timescales to form surface cracks, and hence research was focused on analysis of exposed metal coupons with various surface finishes of alloys relevant to the nuclear industry (i.e., 304SS, A600, and A690). This research revealed unique insights into the corrosion of high Cr, Ni base alloys, specifically that in PWR water conditions at 360°C a continuous, protective chromia layer is not formed, but instead penetrative, filamentary oxidation was observed. This penetrative oxidation has characteristics of internal oxidation, which is typically only observed in metals exposed at high temperature in air. Using a combination of SEM, TEM, and APT, we were able to determine the three-dimensional structure and chemistry of this unique oxidation, and ongoing experiments are providing new insights into the oxidation front and how this penetrative oxidation occurs. Understanding how and why oxygen diffuses through this alloy and why it is not observed in lower chromium alloys provide a novel understanding of SCC and crack initiation.

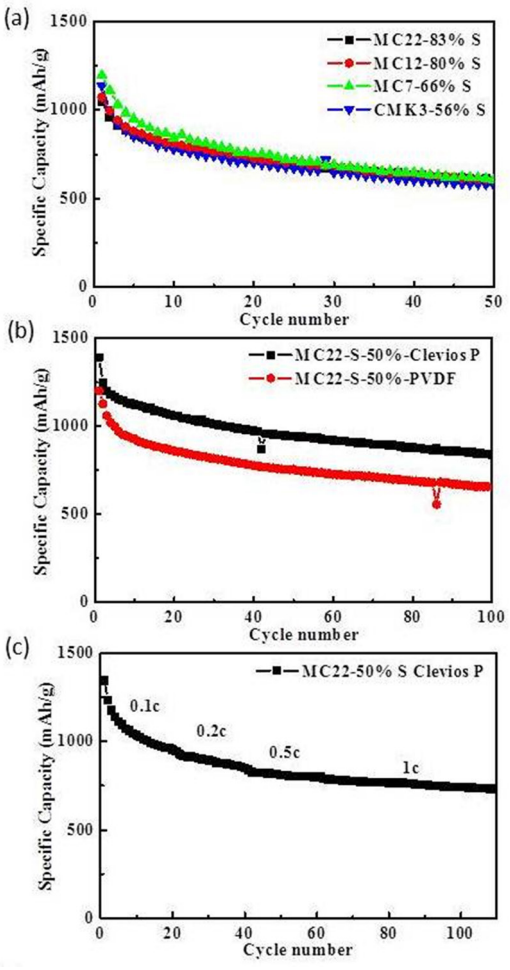
Three-Dimensional Structured Composite Nanomaterials for Energy Storage

Xiaolin Li, John P. Lemmon, Jiguang (Jason) Zhang, Jie Xiao

◆ Lithium batteries with high capacity and good cycle stability are key enabling technologies for next generation energy storage devices to accomplish DOE's targets for transportation power supplies. Developing new three-dimensional structured composite nanomaterials will bring revolution to electrode materials and structures and therefore assist with the advancement of lithium batteries. ◆

Currently, lithium sulfur (Li-S) battery is a promising technology with high theoretical specific capacity. Unfortunately, it suffers from extremely poor stability due to the dissolution and shuttle effect of polysulfide anions during charge/discharge cycles. Three-dimensional structured composite nanomaterials will integrate electroactive material, mechanically stable buffer material, highly conductive material, and capping material into an organized architecture in which the individual components will contribute to the desired properties while maintaining the integrity of the overall structure. Therefore, it is important to develop three-dimensional structured composite nanomaterials for these batteries.

Specifically, the integrated three-dimensional structure can possibly alleviate or even eliminate potential shortcomings of nano-components, such as side-reactions that may negatively affect the device performance and cause safety issues. Remarkable advantages include 1) improved structural and mechanical stability for longer life and satisfied safety, 2) enabling new electrochemistry reactions not possible in bulk materials, leading to large working voltage and multi-electron transfer per redox center for higher energy density, and 3) short electron/ion transport distance and large surface to contact with conducting frames for faster charge/discharge rate.



(a) Cyclibility of MCS composite cathodes with different pore sizes. Pores are fully filled by sulfur, (b) Cyclibility of MC22 with 50 wt.% sulfur loading and different surface modification, and (c) Rate performance of the MC22-S composite electrode with 50 wt.% sulfur loading and Clevios P modification.

This project will focus on developing economic synthesis, assembly, and integration approaches that enable cost-effective production of desirable three-dimensional applications and fundamental understanding of the roles of each nanomaterial component and their interfacial interactions. PNNL has made significant investment in energy storage and has developed strong programs in Li-ion batteries, Na-beta batteries, and redox flow batteries. This new Li-S investment is critical for energy storage technologies beyond Li-ion batteries and for breakthrough concepts in inexpensive, large-scale energy storage. Our work has resulted in the filing of a provisional patent application.

In FY 2010, we synthesized an ordered sandwich structured graphene-sulfur nanocomposite as cathode materials for the Li-S battery. The designed structure has a layer of few-layer graphene sheets and a layer of sulfur nanoparticles integrated into a three-dimensional architecture. Making full utilization of the efficient physical and electrical contact between sulfur and the large surface area, the composite highly conductive grapheme provides a high loading of active materials of around 70%, a high tape density, and a high power Li-S battery with the reversible capacity. Coated with a thin layer of cation exchange Nafion film, the shuttle of polysulfide anion from the GSS nanocomposite was effectively alleviated, leading to a reasonable cycling stability of 75% capacity retention over 100 cycles. Transition metal sulfide based nanocomposites were also investigated as materials for Li-based storage devices.

In FY 2011, we synthesized a series of mesoporous carbon (MC) materials with tunable pore sizes (from 3 nm to 22 nm) and pore volume (from 1.3 cm^3/g to 4.8 cm^3/g). We systematically investigated their application as a conducting matrix to incorporate sulfur into the Li-S batteries. Specifically, we elucidated how the pore structure, sulfur loading, and surface modifications affect the

electron and mass transfer in electrochemical reactions, which in turn affect the performance of Li-S batteries. MC materials with a larger pore volume provide higher maximum sulfur loadings, but the battery performances for different mesoporous carbon-sulfur (MCS) composites are strikingly similar when the pores are fully filled by sulfur. An initial capacity of ~1100 mAh/g and capacity retention of ~600 mAh/g over 50 cycles was obtained. We found that partial sulfur filling and surface modification can lead to improved battery performance by promoting the electrical contact between sulfur and MC, thereby reducing the dissolution/diffusion of polysulfide anions and steady supply of lithium ions. Based on this understanding, we designed an MCS composite using large-pore-volume MC (22 nm, 4.8 cm^3/g), controllable sulfur loading (50 wt.%), and a novel Clevios P coating. A discharge capacity of ~1400 mAh/g, stable cycling with capacity retention of ~750 mAh/g over 150 cycles and good rate performance were obtained.

For the sodium ion battery, we continued our work in this area from FY 2010 and further optimized the manganese oxide-based nanowires with high crystallinity and homogeneous nanowire structure, which provide stable structure and short diffusion path for sodium ion intercalation/deintercalation.

In FY 2012, we will try to optimize the mesoporous carbon-sulfur composite cathodes from pore structure, sulfur loading level, and surface modification to further increase the cyclibility. We will also try to optimize the graphene-sulfur sandwich composite cathode by using better surface modification to alleviate the capacity fading. We will develop other methods such as using electrolyte additives and protecting the lithium metal anode, and other methods to improve the cycle stability. Finally, we will attempt to build a full cell with the best composite cathode and protected lithium anode. Ultimately, the success of this project will enable high capacity and low cost energy storage devices for transportation and stationary.

Mathematics and Computing Sciences

A Distributed Systems Architecture for the Power Grid

Jenny Yan Liu, Yousu Chen, Shuangshuang Jin, Mark J. Rice, Ian Gorton

◆ This project will develop an approach for designing domain-specific distributed system architectures for designating computing centers at specific locations in the power grid. The architecture design will be driven by a method and software tool to evaluate the alternative designs qualitatively. ◆

The substantial growth of high quality sensors provides a comprehensive view of the entire connection of the power grid. With this sensor data and high performance computing (HPC), a revolution in the operations of the power grid, namely real-time operations, becomes possible. The key to leverage these benefits is keeping up with the pace of high frequency samples generated from these sensors. To mitigate computing delays of models in the power grid, designating appropriately located computing centers equipped with HPC capabilities creates distributed systems architecture challenges at several levels. Renewable energies may introduce significant variability to state estimation models; however, the impact of geographical location of such a technology remains unknown. All create intricate architecture challenges that must consider factors such as geographic locations, the hierarchical nature of data collection and monitoring functions, requirements from operations such as tolerance for delayed or missing data, and business constraints pertaining to proprietary data, privacy, and organizational boundaries.

Our research project develops a distributed systems architecture that plans the location of HPC platforms to connect decentralized electric power applications and forms the guideline of distributing power applications to meet real-time requirement of critical operations and controls in the electric power system. Being able to integrate HPC platforms with decentralized power applications will significantly improve the computing capacity and efficiency of control systems used in the electric power system. The solution runs individual state estimators in parallel and uses middleware to communicate the intermediate data at real-time among distributed state estimators. The architecture can invoke applications in any language or protocol to transfer measurements from devices at substations to the Energy Management System at control centers. Additionally, the architecture can partition and distribute centralized functions to HPC clusters optimally to reduce communication overhead, given geographical and operational constraints.

The deliverables of this project form a testbed to configure decentralized power applications in an evolving distributed power gird for real-time analysis. Our major accomplishment for FY 2011 is a conceptual architecture design specification for decentralized power applications that can run on HPC clusters. The architecture has the following features:

- Provides an interface that wraps power application code (such as the parallel code of state estimation) to communicate data through any protocol and any message schema.
- Supports unique identification of any distributed applications and data source in the power grid using a Unified Resource Locator.
- Supports hierarchical functions of power applications to communication data through middleware.
- Provides software to divide the power systems automatically based on specified tie lines when distributing the computation of the state estimators.
- Provides software code to divide one large-scale power system into subsystems and allocates the computation to HPC clusters.

The conceptual design of the distributed systems architecture was published in the Proceedings of the 23rd International Conference of Software Engineering and Knowledge Engineering in July 2011.

In addition to the design specification, we also prototyped a test case as decentralized state estimation to validate the design aspects. Based on our literature survey, current research focuses on the algorithm itself but lacks of actual implementation and evaluation in a distributed environment. The prototype of this test case is in a timely manner to the research field. We have selected IEEE 118 Bus System that represents a portion of the American Electric Power System (in the midwestern United States) and deployed a testbed to run decentralized state estimation on PNNL clusters. Different partition scenarios have been tested. We have also measured the communication delays introduced by the architecture inside the Lab network.

In FY 2012, we will develop representative network simulation cases to evaluate the impact of geographic distance and network topology on the communication delay. The simulation outputs will be the inputs to the power grid partition method in order to optimize the communication cost. We will continue the development of other test cases from the distributed power flow to validate the architecture. Based on the observations from test cases, we will develop a performance analysis method to model the architecture runtime behavior so that performance characteristics can be estimated and implement "what-if" analyses when the size of the power system scales and the power applications evolve.

A Multi-Modal Integration Framework for Chemical Imaging

Kerstin Kleese van Dam, James P. Carson, David E. Cowley, Daniel R. Einstein, Andrew P. Kuprat, Dongsheng Li, Guang Lin, Yan Liu, Jian Yin, Eric G. Stephan, Patrick R. Paulson, Abigail L. Corrigan

◆ This project will deliver an open, multi-modal integration framework for chemical imaging that will allow the fast and precise analysis, comparison, and integration of experimental results from many different imaging technologies against the background of exponentially growing data volumes, acquisition rates, data complexity, and an increasing need for real-time analysis. ◆

Today's scientific challenges such as routes to a sustainable energy future, materials by design, or biological and chemical environmental remediation methods are complex problems that require the integration of a wide range of complementary expertise to be addressed successfully. Chemical imaging methods can hereby offer fundamental insights for their solution. However, new experimental technologies have resulted in an exceptional growth in data volumes, acquisition rates, and complexity, presenting researchers with significant challenges, foremost how to manage and analyze effectively the results of their research both for single experiments and increasingly across different investigative methods.

While there is a wide range of analysis tools for single imaging techniques, these were often designed in a different era and are now struggling to cope with the increasing data volumes. Co-analysis of results across different imaging modalities is rarely carried out today due to a lack of support and tools for this type of work. Any existing examples rely on ad-hoc solutions that are not transferable or available to others. This project proposes to develop an open framework for individual and co-analysis of experimental results, with a particular focus on modular solutions that are well integrated with each other and that will scale with the increasing data volumes.

To guide the initial design and development work of the project, the team assessed other chemical imaging LDRD projects and their general workflow and specific requirements. This project refined its architecture outline, defining much more detailed exemplary workflows for the image analysis and visualization, depending on different instrument types. In FY 2011 this project focused on the characterization, potential automation, and speed up of single modality analysis workflows.

For the proof-of-concept, we chose two example experiments that exemplify the two different workflows identified during the initial requirements gathering, thus displaying different characteristics that are common among a wider range of experiments. The project addressed the required design and implementation of the overarching infrastructure as well as specific exemplary applications within the framework for core functionalities required by many image analysis workflows. The multi-modal framework uses the Information Catalogue (ICAT), an existing metadata storage system, in conjunction with an additional semantic store for unstructured metadata collection and storage of structured metadata. The prototype framework includes a number of specific tasks, as provided below.

- Developing a proof-of-concept ICAT client using JavaScript/AJAX for ingestion of data into ICAT (the existing user interface only supports queries).
- Mapping of PNNL business system fields to fields supported by ICAT for automated metadata capture.
- Developing a metadata requirements use case, in which datasets generated for a chemical-imaging workflow will be tagged by their relationship to the overall workflow.
- Provisional selecting of a subset of XML Schema as a metadata specification language.
- Creating an Web Ontology Language (OWL) ontology derived from the XML schema used to describe ICAT datasets. This ontology can be used to support OWL and SWRL (Semantic Web Rule Language) rules to infer metadata requirements based on basic ICAT input fields.
- Obtaining a virtual machine to host ICAT and web interface tools; PNNL recently purchased a site-wide Oracle license that can be used to support ICAT.
- Applying MyEMSL and client use cases to the data model, which help us to identify and make enhancements to fulfill user requirements. Ongoing interaction with EMSL continues to coordinate with them on metadata storage with secure scientific database storage.
- Specifying web services that can automatically infer and deliver XML Schema for additional metadata requirements based on ICAT inputs and a refinement of the user interface for data ingestion.
- Applying MyEMSL and client use cases to the data model, which help us to identify and make enhancements to fulfill user requirements. Ongoing interaction with EMSL continues to coordinate with them on metadata storage with secure scientific database storage.

- Specifying web services that can automatically infer and deliver XML Schema for additional metadata requirements based on ICAT inputs and a refinement of the user interface for data ingestion.

MeDICi was used for the data and software integration to take data from one technique, tool, or application and feed it into another during the workflow execution. The development of the MeDICi software modules is synergized with software tool development on use case 2, including: 1) moving raw image data from the archive drive to the desktop application called Yamfs for transforming the data format, 2) querying out the values of variables of interest for processing, and 3) visualizing the large data sets (over 200 MB) for each file. The data transformation and visualization software are disparate in terms of application programming interfaces (APIs), running platforms and environment, and acceptable data formats. In addition, data flow is quite large for the data transformation and visualization software to handle the data exchange in between.

Moving data from the field to the operational environment requires advanced management and analysis capabilities.

An initial implementation of the two end-to-end workflows for both use cases was started in mid-summer and is expected to be completed in the fall. Next to the framework itself, the project is developing multiple core application components.

Image compression. Entropy-based data compression was applied to mass spectrometry data sets. The compression scheme involves predicting the data distribution and then encoding the data with entropy-based algorithms. We are evaluating options in each step based on both compression ratios and computation overhead.

Image reduction. The project used correlation function, linear path function and other statistical function to extract statistical information from the sample images and evaluated the applicability of other data reduction schemes, including principle component analysis (PCA) and factor analysis for chemical imaging data. In addition, the project assessed whether these schemes can be implemented with acceptable performance and if they can handle the scale of large chemical images.

Segmentation. Segmentation algorithms must be general and intuitive for the non-expert to utilize them. To be effective in the field, the algorithms must also exhibit real-time performance. Accomplishments to date include developing an advanced suite of tools for segmentation based on energy minimization with Graph Cuts, Random Walks, and the PowerWatershed framework.

Registration. Registration approaches allow the spatial organization to represent accurately the relationship between structures and their material or biological products. In addition, in many experiments, subsequent data simulations and calculations exist in unstructured grids. To address this need, we developed image-to-grid mapping codes and are continuing to work on their parallelization.

Visualization. Visualization development focused on an open-source multi-platform solution that supports parallel processing: Paraview. We have installed and tested Paraview running in parallel on multiprocessor client and server systems. We carried out proof-of-concept visualization and segmentation in Paraview for both project 1.1 and 2.2. A proof-of-concept Programmable Python Filter was also developed.

During the year, the project team had a range of publications, including one submitted and two published journal articles, a book chapter, and a number of invited talks at national and international meetings and workshops.

For FY 2012, the project will deploy the initial single instrument workflows for user testing and feedback. This should enable faster and advanced analysis capabilities and the analysis of much larger data volumes. Further, the project will start to address the critical co-analysis of results by developing the necessary components and workflows. In addition the critical work of generalizing and formalizing of such co-analysis workflows will begin, enabling the inclusion of further modules from other contributors for which the project has already a number of interested contributors.

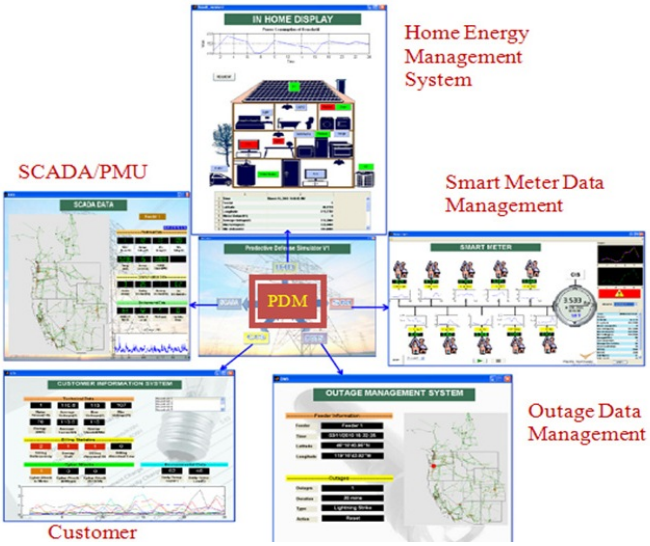
A Predictive Defense Model for the Smart Grid

Ning Lu, Mark D. Hadley

◆ It is critical to modernize our national electricity transmission and distribution grids while maintaining a reliable and secured electricity infrastructure. This research builds innovative and unique capabilities that bridge the critical gaps between data rich and information rich and between smart and secure to make sure that security is built into the smart grid from the beginning. ◆

Traditionally, corrupted measurement data and outliers are detected and discarded without being analyzed to identify whether they are caused by random equipment failures, unintentional human errors, or deliberate tempering attempts. In addition, data collected from different channels are rarely cross-checked for data integrity based on redundancy, dependency, correlation, or cross-correlations, which reveal the interdependency between data sets. Thus, cyber attackers can remain undetected for a long time until their attacks lead to widely spread data collection failures or data errors that may take the grid down. The massive use of low-cost communication and electronics provides an explosion of information that bears different data formats, timestamps, with/without secured information interchange mechanisms. However, the smart grid is at its beginning stage with a yet-to-be designed predictive defense supervisory system that can efficiently process myriads of data to evaluate the status of the system, identify failures, predict threats, and suggest remediations.

The innovation behind this research is the detection-in-depth process of information by dynamic filtering, multi-layer triggering, and cross-diagnosis to identify the nature of system events and incidents as security vulnerabilities in personnel, technology, or operation. Then, response can be taken effectively. This LDRD project targets the development of a predictive defense model (PDM) for the smart grid that that detects physical and cyber threats, predicts the likelihood of the threats, and aids the grid operator to take proactive actions to remove, prevent, or mitigate the threats.



I2MS prototype design. The user interface serves as a gateway to multiple data sources in a smart grid operation environment.

In FY 2010, we finished design considerations, physical and information network configurations, data flow generations, detector selection and placement, and testing results of a distribution grid testbed that allows researchers to design and test integrated information management systems. The test system models the interdependency and correlation among different data sets and provides an environment that closely resembles actual data collection systems. It provides us with a cheaper yet effective tool to evaluate the performance (such as hit rate and false alarm rate) of an integrated information management system (I2MS) in anomaly detection.

In FY 2011, the first phase of the project focused on setting up a smart distribution grid testbed to test or compare designs of I2MS. The second phase study was focused on demonstration and evaluation. The following tasks have been completed this year to accomplish our objectives.

A Prototype I2MS Design. A prototype was built to demonstrate how I2MS is designed and how it performs. Each modeled entity represents an information layer, and the major modeled entities in the prototype are the smart meter network, the supervisory control and data acquisition (SCADA), the phasor measurement unit (PMU) and the outage management system (OMS) Layer, the Utility customer information systems (CIS) Layer, and home energy management system. A centralized decision-maker "detector" examines the individual data sources for abnormalities. Then the detector cross-checks the synthesis of data sources to identify the cause and to determine the appropriate response. The data for all data sources were either generated from experiments or selected from typical data sets through simulations with cross-correlations and interdependency preserved.

Scenario settings. In an I2MS environment, abnormalities can be simulated. An abnormality can have several possible causes, like bad weather, equipment failure, cyber attack, and energy theft. For example, in energy theft scenario, the smart

meter reading saved in "baseline" is manipulated. Several abnormal phenomena (or data corruption) have been developed for investigation:

- Energy bill is significantly lower than average
- Electricity consumption of neighboring households is higher than normal
- Electricity consumption pattern is irregular
- Energy consumption deviates from its past patterns
- Outage rate of the tampered smart meter is high
- Communication package from the tampered smart meter can be easily lost
- No energy discount issued to the customer.

Test results. A main feature of an I2MS design is that it gives operators the ability to detect the altered situations, and provides mitigation guidance. After scenario setup, the corresponding data set will be examined by "detectors." The question is whether we can identify the scenario by looking at the tampered data set. Essentially, the reasoning process built into detectors uses a series of logic steps as a descriptive means for determining the interdependence between data and different scenarios and calculating probabilities. The logic process is adaptively changed to reflect different operation conditions (e.g., seasonal variations). The most likely cause for the tampered data received is bad weather, while other events like cyber attack or energy theft are not possible.

The benefit of an investment in smart grid infrastructure is the availability of high resolution data collected from more measurement points. To monetize the benefit, information that can facilitate the grid operation, maintenance, and planning needs to be extracted from these data sets and made available to grid operators in an actionable manner. A testbed that can model information flows is therefore important to test and benchmark the performance of information management systems.

A Prototype Systems Biology Knowledgebase Platform

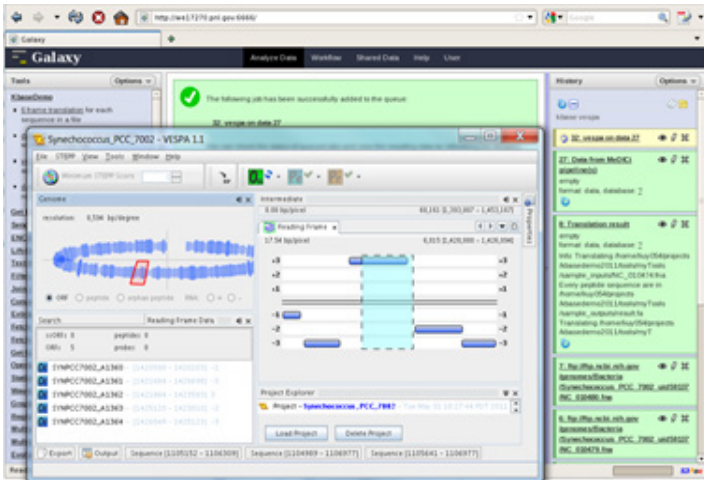
Ian Gorton

◆ The aims of this project are to design, integrate, and demonstrate various advanced computer science techniques in the context of a systems biology knowledge base (Kbase). Specifically, these are data-aware pipeline executions in a federated cloud infrastructure and advanced semantic data harvesting and capture that will enable biologists to search across federated Kbase sources to locate data of interest. ◆

Systems biology is characterized by a large community of scientists who use a wide variety of fragmented and competing data sets and computational tools of all scales to support their research. To provide a more coherent computational environment for systems biology, we are working to design a Kbase that is created on a federated cloud-based system architecture. The Kbase could eventually host massive amounts of biological data, provide high performance and scalable computational resources, and support a large user community with tools and services to enable it to utilize the Kbase resources.

In this project, we have explored specifically how existing bioinformatics workflow tools can be extended to exploit the distributed, cloud-based data and computational resources that will exist in the Kbase. We have aimed to provide support for workflows in as transparent fashion as possible, so that users remain unaware of the underlying complexity of the Kbase. This is a crucial requirement for the rapid uptake of the Kbase technology by the user community. We also worked with biologists to define a typical workflow that is highly representative of those that the Kbase will support based on the genome annotation process, which aims to analyze proteomic data from environmental samples of microbial communities. To cover sufficient breath of the analysis, it is most informative to evaluate the peptides from the proteomics sample data against both fully sequenced genomes (such as DNA sequence files published from GenBank) and unassembled open reading frames obtained from metagenomic analyses. Based on the experimental evidence and analysis results, biologists can curate a published genome annotation and make new research contributions to the community.

The workflow starts by retrieving genome data relevant to a microorganism under study from GenBank. This becomes input into the six frame translation script that produces the possible set of peptides for encoding by the genomes. Next, these possible peptides, along with the relevent proteomics data, form the inputs for the Polygraph application, a statistical peptide identification program. Polygraph executes statistical methods combining a database and spectra library search for matching peptides from experimental data results identified from a biological sample, and implemented using the Hadoop service on the NERSC Magellan Cloud to provide a scalable, high, performance analytical tool. Polygraph outputs, a list of peptides and their possibilities, are then fed into a desktop-based visualization tool that shows these peptide sequences aligned with genome sequences so a biologist can examine and refine the peptide identification. To implement this workflow, we built extensions into the Galaxy workflow tool from Pennsylvania State University that is widely used in bioinformatics. These extensions enable us to plug cloud-based processing seamlessly into Galaxy, enabling biologists to exploit these resources without dealing with any additional complexity in problem definition. Behind the scenes, we orchestrate the workflow using our MeDICi technology.



MeDICi gathers and transports input data from Galaxy to the cloud platform, invokes necessary codes on the cloud (in this case, Polygraph), and returns outputs over the network to Galaxy, where it is fed into the visualization tool.

This technology is impactful, as it brings the powerful world of cloud-based analytics to the biologist's desktop, without the need to understand the complexity of running tasks on the cloud. Importantly, the "plug and play" architecture we built is generic and potentially can be used with any workflow tools that have software hooks that support extension. For example, the same mechanisms would work with minor modifications with Taverna and Kepler. In this manner, our MeDICi platform provides a robust and high performance distributed integration framework upon which further innovations in this area can be built.

A Scalable Fault Tolerance Infrastructure and Algorithms with Programming Models and Scientific Applications

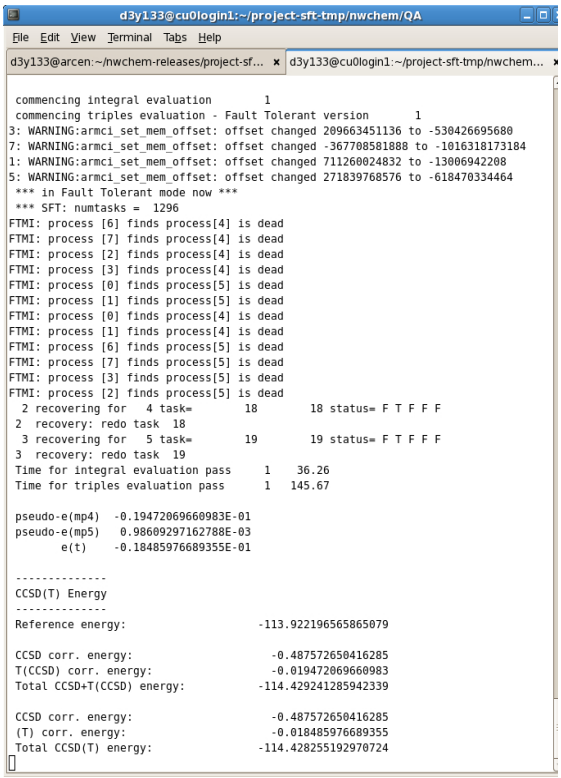
Abhinav Vishnu, Wibe A. de Jong, Hubertus J.J. van Dam, Shuaiwen Song

◆ Delivering fault tolerance on exascale scale computing platforms with millions of processing elements and components will enable leading edge scientific applications to fully utilize the performance of these systems to accomplish scientific discovery and innovation that will transform the Nation. ◆

With the arrival of petascale scale computing platforms and the advent to exascale systems, the high performance computing community is entering an era of combining millions of processing elements and components. Besides achieving peak performance out of these systems, one of the major remaining challenges is how to handle reduced mean time between failures (MTBF) of various system components. Providing fault tolerance to the system software stack is imperative to achieving any realistic goals of sustained peak performance as well as enabling scalable application software to utilize these systems effectively to accomplish leading edge scientific discovery and innovation.

In this project, we are developing a fault tolerance management infrastructure which embodies many components required to provide fault tolerance to the applications. These components include scalable fault detection using hardware mechanisms as provided by the modern systems, low overhead mechanisms of propagating this information to useful entities in the system to reduce the overall cost of recovery and leveraging the infrastructure for hard errors and soft errors. This fault tolerance management infrastructure is being used at multiple layers for vertical fault tolerance across system software used by Aggregate Remote Memory Copy Interface (ARMCI), which is a high performance communication runtime system. The infrastructure is also being used by programming model layers such as Global Arrays. The objective of the project is also to develop high performance and fault tolerant computational chemistry methods such as Coupled Cluster method, which is used in high accuracy calculations. The computational chemistry method requires a fault tolerant Global Arrays, ARMCI and fault tolerance management infrastructure, which needs to be designed and developed for high-end systems which exist today. Specifically, we are adding capabilities to NWChem to handle processor faults and be able to recover from them without using the checkpoint/restart mechanism.

During FY 2010, we developed an initial fault tolerance management infrastructure that provided efficient fault detection, resilient communication protocols, a messaging layer for arbitrary data communication, and a fault tolerant process manager in addition to fault resilient, non-data moving collective communication operations. Using global arrays and ARMCI as the research and development vehicle, we began to demonstrate the fault resilient execution of communication benchmarks with a hard node fault. The fault tolerant communication infrastructure is in publication for the 2010 International Conference on High Performance Computing.



The output of a run on eight processors across four nodes, demonstrating the successful recovery from a single-node failure.

Within NWChem, an approach to building fault tolerant applications using (and on top of) global arrays was designed and implemented to provide required fault tolerant infrastructure to the application. With this infrastructure, a fault tolerant version of the coupled cluster triples was implemented. We performed live demonstrations of our research during review meetings and program managers who visited the lab during this period.

In FY 2011, we developed fault tolerance Infrastructure for Cray Seastar systems in addition to demonstrating fault tolerance capability of Global Arrays and NWChem on the Supercomputing Conference Floor at the PNNL booth. The Supercomputing Conference is a premier conference which attracts 9000+ attendees from across the world.

Cray Seastar is a proprietary network used on ORNL Jaguar system, a supercomputer which has been consistently ranked in top 5 in the system. There were many attributes to the design and development of infrastructure. We designed an infrastructure to detect faults in the system using the primitives provided by the Cray Seastar network. The design choices included hardware notification from the network on failures or using software timeouts to detect a fault. The scale of the system also required to re-visit the actual cost of recovery to be proportional to the degree of failure. To meet this stringent requirements, we designed and developed an adaptive method for fault detection which would leverage hardware mechanisms as much as possible, while using software timeouts when the hardware mechanisms cease to exist. To expedite the cost of recovery, we also designed fault tolerant collective communication primitives which would efficiently broadcast the information with minimal performance degradation. A combination of these capabilities ensured that the cost of recovery is proportional to the degree of failure.

A critical component of the infrastructure is fault tolerant process manager. In the previous year, we designed one for InfiniBand based systems. However, we did not have system software available in open source for Cray. For successful completion of this project on Jaguar systems, Cray's collaboration was critical. Observing the success of our project, Cray designed and implemented a fault tolerant process manager and provided us the software stack for demonstrating fault tolerance. At the same time, we have continued to design and develop scalable fault tolerant methods in computational chemistry using NWChem. We have increased the scalability of fault tolerant NWChem's methods by designing methods for Singles, Doubles, 4-index transformation in addition to Triples energy correction. Our major result is that we can achieve fault tolerance with only an additional memory of 2-3%, insignificant time overhead in the absence of failures and <10% overhead in the presence of failures. Compared the state of the art checkpoint/restart systems, which only allow 85% of the CPU cycles to be available for computation, our proposed solution outperforms them by a very significant margin.

In addition to the above achievements, we also designed a fault tolerance management infrastructure for P7-IH systems which are based on the new IBM proprietary Interconnect. We engaged with IBM on multiple aspects of the Interconnect for efficient fault tolerance and techniques by which the proposed approaches can be used by applications beyond computational chemistry. The proposed research is on-going and as the availability to the system increases, we are likely to be able to complete this during this fiscal year.

Most of the research proposed above considers hard faults, faults in which components become permanently unresponsive. While these failures are increasingly prevalent, there is another class of failures which have seen tremendous increment during last couple of years. Soft errors, transient errors in the hardware logic, may lead to silent data corruption are an artifact of low voltage systems and increased density of integration. In the memory subsystem, they are likely to occur in SRAMs – frequently used for designing cache architecture. State-of-the- art approaches have primarily focused on using iterative methods to circumvent this issue; however, studies have shown that this is not always feasible and may not result in correct solution even after increased number of iterations. We were challenged to design efficient algorithms in time and space, along with program invariants so that we can have high accuracy with minimal data replication and recomputation on the fly. We have designed an approach for Density Functional Theory in computational chemistry focusing on different attributes of data in the computation. We believe that our proposed approach will have a strong impact on the co-design of algorithms in computational chemistry and global address space models, making PNNL a leader in designing fault tolerant applications and programming models.

In FY 2012, we will design a fault tolerance infrastructure for Cray Gemini system, which is available on NERSC Hopper and upcoming ORNL Titan system. We are working closely with Cray to design a fault tolerant process manager and design efficient fault tolerance management infrastructure. We anticipate to have the solution working by the end of the fiscal year to be able to demonstrate our work using NWChem and Global Arrays. We are also planning to integrate our proposed research with open source releases in Global Arrays and NWChem for broader usage in the community. A significant portion of the research would also be focused on designing fault tolerant methodologies for soft errors. Soft errors would require a lot of theoretical analysis of the proposed solutions, followed by a detailed empirical analysis. As an example, we would consider different forms of data distribution and various computational chemistry modules to design the best possible fault tolerant algorithms in time and space. Some of these modules are used in multi-phase manner which imposes additional challenges of data flow from one module to the other. We also intend to study the impact of soft error on various data structures. For example, a data structure which is read only is less likely to propagate the impact of soft error than a data structure which is updated frequently and also read on other iterations. Similarly, the impact of a bit-flip in Most Significant Bit versus Least Significant Bit will have altogether different results. The challenge is to come up with program invariants that can capture the impact of frequently used data structures in the application. We intend to achieve these objectives during the upcoming fiscal year.

Adaptive Cyber-Defense Using an Auto-Associative Memory Paradigm (ACAMP)

Ryan E. Hohimer, Frank L. Greitzer, Shawn D. Hampton, Patrick R. Paulson, Christine F. Noonan, John R. Schweighardt

◆ This project created an advanced method of pattern recognition in cyber streams, enabling more advanced reasoning processes to be applied to the threat assessment process. ◆

The trend in software exploits is changing from operating systems to application software, and the list of potential exploits is rapidly growing along with the application space. Hackers can take advantage of this trend, as it provides a large library of exploits to use to gain access, traverse, manipulate, and pilfer. At the same time, the insider threat to an organization's intellectual property, personnel, client records, and other assets has been recognized as one of the top security threats facing information systems. The initial application focus for the ACAMP LDRD was in the cyber security domain to include malware or other external exploits and a focus on the insider threats.

This research is visionary in its employment of a conceptual model informed by a functional mimicry of the neocortex—the ultimate pattern recognition system—that seeks to develop an unprecedented dynamic, adaptive cyber defense system that can reason across multiple, diverse data domains to yield more comprehensive automated support for detecting and recognizing patterns in high-risk "triggers" to help focus the analyst's attention and inform the threat analysis process. The domain-independent design of the reasoning system enables potential applications to diverse problem domains.

Current practice in monitoring and mitigation of the insider threat is reactive in nature; cyber analysts must perform manual review and correlation of data in diverse data sets and cyber logs to attempt to recognize patterns of malicious behavior. Our envisioned approach to development of a hierarchical system of reasoners that excels at correlating information across multiple data domains is uniquely well-suited to address the insider threat problem. Building upon the reasoning framework designed in the first year, we developed the *CHAMPION* reasoning system – designed to perform *"Columnar Hierarchical Auto-associative Memory Processing In Ontological Networks"* – based on an inspirational metaphor of the functional organization of the human neocortex. CHAMPION uses a predictive modeling framework that integrates a diverse set of cyber domain data sources that may underlie malicious insider exploits. This comprehensive threat assessment approach provides automated support for the detection of high-risk behavioral "triggers" to help focus the analyst's attention and inform the analysis.

Following the neocortex design metaphor, the functional requirements for *CHAMPION* include:

- Process input from multiple and diverse sensors (data sources)
- Create and store sequences of patterns to raise the level of analysis beyond individual/isolated data to enable the system to identify behavioral patterns
- Store the sequences of patterns in invariant forms to enable system functions that support adaptation and generalization capabilities
- Recall sequences of patterns auto-associatively to produce dynamic detection capability within a "memory-prediction" framework
- Store the sequences of patterns in a hierarchy to facilitate growth and "learning" functions of the reasoning system.

The processing unit of the neocortex is the cortical column; for the *CHAMPION* reasoning system, the basic processing unit is referred to as the Auto-associative Memory Component (AMC), which mimics the functionality of the cortical column. The hierarchical organization of the AMCs enables integration of the analysis and reasoning process across different domains of data.

A basic premise is the separation of the domain knowledge from the reasoning framework. This allows the system to be domain independent, applying to a variety of threat and warning analysis or "sensemaking" problems without modification of the reasoning components per se. The domain knowledge is captured in ontologies that drive the reasoning components; ontologies therefore represent specialized domain knowledge necessary to reason about the data. Unlike conventional graph-based knowledge representations that require reasoning over the entire graph, the CHAMPION hierarchy of reasoners comprise a collection of AMCs such that lower-level AMCs feed higher-level AMCs; outputs from the AMCs produce the graph structure dynamically, as data are analyzed. This yields a belief propagation network that performs transformations of low-level, literal inputs (which might correspond to outputs of anomaly detectors in distinct data domains) into higher level abstractions to which higher level cross-domain information fusion and reasoning are applied. Such highlevel information fusion and analysis are

typically lacking in conventional threat monitoring/ detection systems, which impose a greater information processing burden on the human analyst.

This research advances the state-of-the-art in model development and reasoning system design in two key respects: the system design uses an innovative hierarchical network of reasoners, and the reasoner design extends traditional case-based reasoning to yield knowledge-intense case-based reasoners (KI-CBR), which are themselves enhanced by modifying the traditional reasoning cycle to include analysis of invariant forms of stored patterns (i.e., patterns previously gained from experience or elicited from domain experts). We chose to alter the traditional case-based reasoning (CBR) cycle because the iterations through the case library to find an exact match do not fit our functional requirement to use an invariant form to characterize solutions. Thus, in the CHAMPION CBR cycle, as a new problem case is considered, it is compared to semantic expressions to see if it qualifies (i.e., belongs to the appropriate class) to be in the case library. A Description Logic reasoner is used to examine the state of the new case: if that state specifies that the classification is true, the new case is added to the case library and published to the working memory knowledge base.

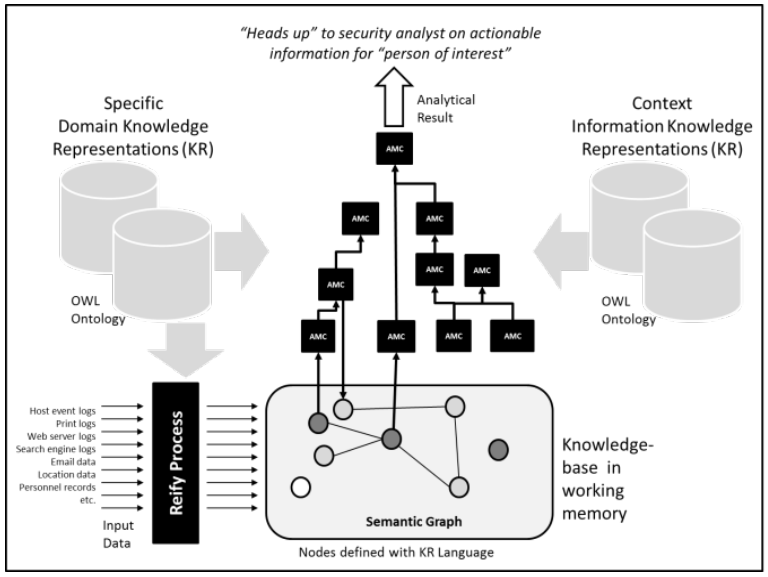
The domain independence of the CHAMPION system is demonstrated by the fact that it is being applied in a variety of application contexts. Originally implemented for external cyber threat analysis, the focus turned to insider threat in the second year. The CHAMPION reasoning framework is being applied in threat analysis application domains beyond cyber security: a) one application context is the detection of malicious exploits to perturb power grid consumer data reflecting energy usage—a predictive defense/Multi-layer, Data-driven Advanced Reasoning Tool (M-DART) for smart grid integrated information systems was proposed and is being funded as a separate project, b) another proposed CHAMPION application, pending client funding, is a weapons nonproliferation threat analysis application that models the nuclear fuel cycle.

Accomplishments and products of our research during FY 2011 include the following developments:

- Continued the development of the KI-CBR technology and auto-associative features of the ACM components of the model.
- Continued system implementation using an agile development approach that produced a robust implementation of the CHAMPION system, suitable for deployment in an operational environment .
- Developed ontologies for selected knowledge elements in the insider threat application. Working closely with Laboratory cyber security and counterintelligence staff, we built ontologies that support analysis of multiple data sources to reveal patterns of risk elements (or "intersecting anomalies") that are not otherwise apparent in conventional analysis of separate data logs.
- Implemented a proof-of-concept operational deployment of an insider threat monitoring/decision support application for use internally by unclassified cyber security/counterintelligence personnel.

We presented many briefings on this research and wrote two peer-reviewed scientific papers describing the research (one paper has been published in a journal; one paper has been submitted to a conference and we are awaiting notice of acceptance).

In summary, we developed a new approach to computational reasoning that combines key aspects of belief propagation networks, CBR, semantic web and Description Logics to yield a "memory-prediction" framework that is functionally modeled after the neocortex pattern recognition process. Implemented as a hierarchy of reasoning agents, this domain-independent CHAMPION system may be applied to a variety of decision-making problems. Our research has led to a paper published in the *Journal of Strategic Security* and a submitted conference paper.



CHAMPION framework in an insider threat monitoring application.

Adaptive Multi-Signature Network Analysis System

Mary E. Peterson, Adam R. Maxwell, Michael G. Foley,
Patrick G. Heasler, Alex J. Stephan, Jerry D. Tagestad

◆ This project is developing techniques to detect, classify, and track small boats, combining acoustic, image, radar, and other sensor data to enable tracking of a particular target. We envision multiple uses for these techniques, including interdiction of illicit traffic in drugs or people, and land or water search-and-rescue efforts. ◆

Persistent multi-sensor systems have the ability to enhance significantly threat detection, classification, and interdiction. Of practical consideration is that the deployment of overlapping multi-sensor systems for wide area coverage will not be technically or economically feasible. The primary scientific challenge becomes developing the multi-sensor spatial analysis technique(s) that incorporates data from multiple network sensor systems that are not necessarily co-located; associating features collected from multiple sensors with a specific target; enabling the identification, reacquisition, and tracking of the target as it moves in space and time; and stochastically predicting the movement of the target. One technical gap has been the lack of a multi-sensor data set, such as two multi-sensor systems – one stationary and one mobile – to collect and characterize individual sensor signals to identify unique signatures for classes of small maritime vessels. These multiple network sensors are sparsely located and not overlapping. This effort has generated a significant, multi-sensor data set for a large variety of small maritime vessels traveling in and around the Pacific Northwest. Real-time analysis of such large multivariate data streams remains a critical capability gap.

	1	2	3	4	5
1	***1.00***	0.00	0.00	0.00	0.00
2	0.00	***0.93***	0.00	0.00	0.07
3	0.00	0.00	***1.00***	0.00	0.00
4	0.00	0.00	0.00	***1.00***	0.00
5	0.00	0.07	0.00	0.00	***0.93***

A confusion matrix showing the misclassification for five small recreational boats, based on a combined acoustic and image signature. A value of 1 indicates perfect classification, and a value of 0.93 indicates correct classification 93 percent of the time. This error rate is an improvement of 25 to 30 percent over using acoustic or image-based classification alone.

Significant work has been done with networks of sensor nodes and in multi-modal sensor classification of targets. Typically, such nodes must have overlapping spatial coverage in order to track moving targets, as the signature classes only provide broad categories such as "large ship" versus "small boat," or "gasoline-powered" versus "diesel-powered" boat. Developing the analytical capability to process such multi-sensor data sets in real time, our approach focused on three areas: 1) feature extraction to construct a signature from disparate sensors, 2) detection of the target of interest in a relatively noisy environment, and 3) development of multi-sensor geospatial techniques to track targets. We are working to develop an analytical system that can use data collected from multiple network sensors to recognize signatures for individual moving threat entities in real-time and integrate and project their movement tracks to facilitate interception/interdiction.

We used currently unexploited details in a multi-sensor signature to enable tracking of targets without overlapping sensor node coverage, to allow more cost-effective monitoring of a broad area. We used an extensive small boat database collected by PNNL under a previous program to accomplish this. Our initial goal was to determine the effectiveness (error rate) of our hypothesized signature, and how it will degrade over time or because of changes in the environment.

We developed a signature for a set of small boats using hydrophone and camera sensor data to create a feature vector consisting of acoustic signal-to-noise ratio at several characteristic propulsion frequencies, and the silhouette of the boat. In addition, we developed a Bayes classifier to test the error rate of our signature to see how well we could distinguish particular boats. We were able to classify boats on this basis using either acoustic or imaging sensor data and demonstrated a significant improvement in classification by considering both sensors. The average error rate was 3 percent when using both sensors, which is a surprisingly low, considering the difficulty of the problem. Key findings of this research were first, that a viable signature appears to exist for small boats using acoustic and imaging sensors. We found that combining multiple sensor types can significantly reduce error rate. Additionally, we learned that we can quantify error rates in classification using statistical techniques.

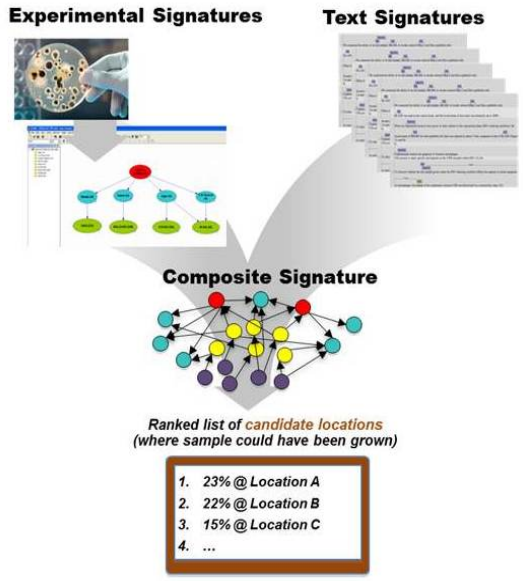
This effort will provide the foundations and for identifying and detecting targets in real time using a network of multimodal sensors that are not necessarily overlapping in spatial coverage.

Advanced Statistical Network Models for the Integration of Experimental and Open Source Textual Data for Bioforensic Analyses

Bobbie-Jo M. Webb-Robertson, Courtney D. Corley,
Helen W. Kreuzer, Lee Ann McCue, Liam R. McGrath

◆ This project is developing a statistical methodology from composite signatures to identify the origins of biological samples. The results will reduce the time it takes to identify the origin of samples, which can increase the speed of prosecution. Our research also presents a novel approach to extract environmental factors or determinants from open-source literature. ◆

The integration of disparate data into robust signatures is necessary for many problems in the intelligence community. Some examples include bioforensic analyses to identify the "location" of a sample origin, authenticating food origins to determine the cause of a contamination, and tracking explosives to their originating location. In all cases, there will typically be sensor-level information that yields clues to the content or composition of the subject of interest. This information alone may be inadequate to determine origin. Integrating with other non-experimental sources of information into signatures would help narrow the investigative field.



The basic framework of Bayesian composite signature generation for the purpose of bioforensic attribution.

This project is developing a computational framework to quantify statistically the identification of an entity (person, place, etc.) associated with the origin of a biological sample through the application of composite signatures. The first set of data includes traditional experimental forensic approaches, including chemical composition to determine culture media, genomic information, and proteomic data. The second set is analytical information about capabilities required to grow the sample and includes results of scientific literature, web searches, and a list of scientists and other personnel associated with the necessary capabilities.

In FY 2011, our work led to three major development creations, which are described below.

Complex Biomedical Event Extraction Pipeline and Open-source Dataset. In the first half of FY 2011, we developed the event extraction pipeline that uses novel signatures composed of traditional linguistic features and semantic knowledge to predict event triggers and their candidate arguments. In the second half, the developed pipeline was leveraged to search scientific publications for specific types of culture media. A random sample of publications about the growth of *Bacillus anthracis* was selected to develop the benchmark dataset. Sections related to attribution and bacterial growth methods (title, abstract, materials and methods) were extracted. To determine what culture media were used by the authors, publications were read and annotated, with this information developing and evaluating text-based and composite signatures in the larger Bayesian framework.

Methodology for the open-source text-based signature generation. The event extraction pipeline was used to generate signatures of each publication in our open-source dataset in simple binary vectors based on the presence or absence of key terms. Using a linear discriminant and given the scientific publication, we accurately predicted the correct culture media 69 percent of the time. A statistical test of the measured accuracy vs. random chance (~14.3 percent) demonstrates that our accuracy is significantly higher than random chance. This statistical prediction model was integrated with open-source literature into the Bayesian framework.

Methodology for composite signature generation. Composite signature generation was derived in a Bayesian framework. The conditional independence of the data streams allows us to integrate the information directly to the final probability of interest P(*PT*|*ED*), which is the probability of a specific publication (*PT*) given the experimental evidence. A statistical linear discriminant model classified ~38 percent of the publications correctly from the integrated signature, which is higher than expected by random chance.

For FY 2012, we will continue refining the text-extraction methods, modify the framework to focus on feature extraction, extend the methodology to data collected for the pathogen *Yersinia pestis*, and identify relationships among authors to improve composite signature accuracy.

Attack Impact on the Electrical Grid as a Function of Network Topology

Garill A. Coles, Artyom Sadovsky, Pengwei Du

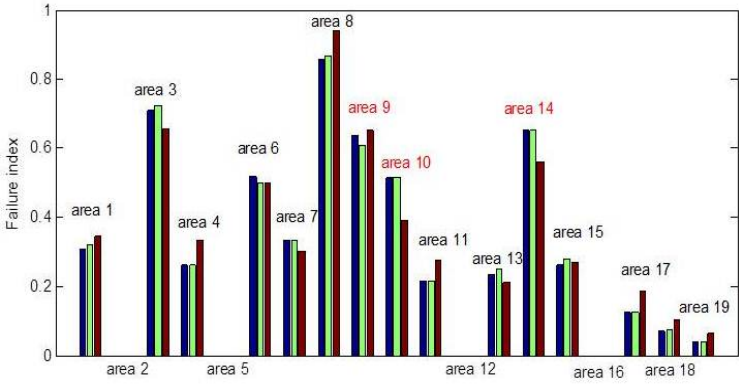
◆ This project investigates a novel method for assessing the vulnerability of the electrical grid to cyber attacks by relating this vulnerability to network topology. This research will lead to metrics that provide grid planners and regulators with a way to evaluate "grid survivability" quantitatively, given an attack or adverse event as a function of proposed changes to network topology of the grid. ◆

The electrical power grid security is managed on an asset-by-asset basis by the registered entities that comprise the North American Electric Reliability Corporation. Consideration of both the increased vulnerability of the grid given an attack on a single asset (grid component) and impact to the grid of an attack on more than one asset (which may be conceivable in a cyber attack) is important to understanding grid security and reliability. Our work is based on previous research about how the topological structure of a communication network determines its ability to withstand a particular type of physical attack and how it can be used to evaluate network classes. Topological changes and planning for the electrical grid are primarily performed by transmission planners with an eye toward improving the efficiency and reliability of the grid. A critical component is defining relevant topological parameters: simply measuring network connectivity is not sufficient, and carefully defining network structure is an important challenge.

The objective of this research was to develop a quantitative methodology and corresponding metric to assess the resilience of different electrical grid configurations to classes of attacks or adverse events. This entailed defining an appropriate way to measure vulnerability, calculating the metric in practice, and demonstrating the calculation for a specific network and attack scenario. Contingency analyses typically consider such factors as areas of network constraint, peak use, and loss or failure of key grid components but do not exhaustively assess the impact of multiple asset failures that might occur from a wide ranging adverse event (i.e., hurricane). Once we characterize important electrical power system topological parameters and define network survivability, we can perform simulations that estimate the survivability of networks of varying configurations following possible attacks.

We began our research by defining a way to assess grid vulnerability. This was referred to as "grid survivability" and was defined as the likelihood that the grid is able to transition from a weakened state (which results from an attack) to a normally functioning state. In turn, this required us to define precisely the terms "weakened state" and "normal state." We defined these phrases in terms of voltage and frequency deviations relative to the voltage and frequency levels found in a normally functioning grid, as the voltage and frequency are primarily indicative of the power quality.

After defining the survivability metric, we employed the commercial software called Positive Sequence Load Flow (PSLF), which is used for grid contingency planning, to evaluate the metric. A full-detailed Western Electricity Coordinating Council (WECC) system model comprising approximately 15,000 buses and 3,000 generators was used in the simulation. Traditional reliability evaluation methods used by utilities are limited by not taking the account the uncertainties in scenarios to be investigated. In this project, this was solved with a Monte Carlo approach, which required us to define classes of attacks along with the relative likelihood of each and implemented by the scripts in MATLAB that would simulate these attacks upon WECC.



Demonstration of grid vulnerability as a function of network topology.

After each simulation, we calculated the frequency and voltage of reversions to a normal network state, which is our survivability metric. As a demonstration of concept, we performed these simulations with respect to several network topologies: first was the unmodified WECC network, second was WECC with the addition of a high voltage north-south transmission line, and third included a high voltage east-west transmission line. These simulations successfully reveal the relationship between network topology and grid survivability while considering uncertainties in attack scenarios. This information is rarely seen by traditional analysis because of inherent complexities in power grid. As this work lays a foundation for understanding of future grid vulnerability, we are confident that future work can employ it to study the effects of a broader variety of topological changes to the grid and extend the proposed framework to study other factors such as communication errors and bad weather effects.

Compressive Sensing for Threat Detection

Nathaniel Beagley, Andrew J. Stevens, Yannan Sun, Heather M. Orr, Chandler J. May

◆ This research aims to improve the ability to detect and predict national security threats. By using compressive sensing algorithms, we are working to improve the efficiency and robustness of signatures that indicate those threats in a noisy environment or during instances when they are purposefully obscured. ◆

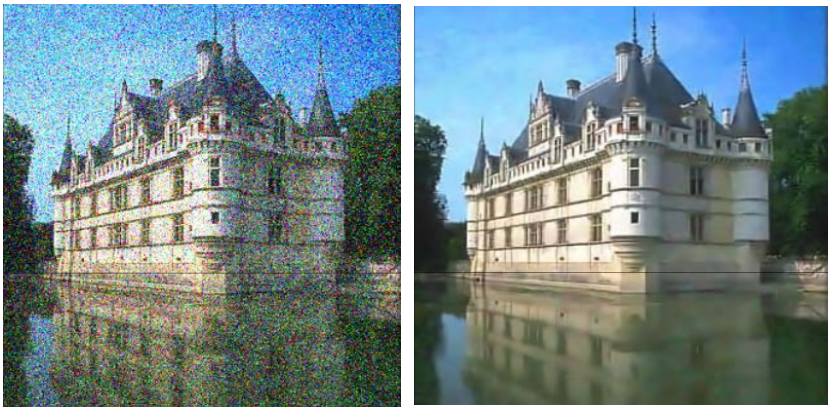
Compressive sensing is class of algorithms that provides methods for reconstructing high-resolution observations or measurements from data streams that are incomplete, degraded, or under-sampled when the data meet certain mathematical conditions. While compressive sensing is a very active research area and has provided groundbreaking results, it has not been fully leveraged in the area of sensor applications and signature detection. Our research quantifies the effectiveness of these reconstruction techniques in the context of signature detection. We are focusing on two areas:

- Detecting signatures from a degraded data set (such as in the presence of noise, interference, or obfuscation). The degraded measurement is reconstructed using compressive sensing, and we determine if the needed features are identifiable in the reconstructed data so that the threat signature can still be detected.
- Detecting signatures in time-constrained and data-constrained environments. In both cases, the sensor is capturing less data (i.e., lower resolution measurements) than in normal operation. We will quantify the level to which we can lower the data collection rate and still detect the signature after reconstruction.

A successful outcome of this work will provide an improvement in the robustness of signatures and an improvement in the efficiency of data capture for signature detection. Additionally, it will provide knowledge of how efficiently noise and interference can be mitigated in an operational scenario and how to best allocate resources when designing sensor and signature threat detection systems.

In FY 2011, we designed and implemented a software infrastructure to run "degradation/reconstruction/signature" experiments. These experiments create and evaluate a large number of test cases. Starting with a normal set of data observations as input, the experiment first *degrades* the observations via noise, interference, or sub-sampling (attempting to match degradation that would occur in an operational environment) with a range of intensities of the degradation. This creates a large number of data samples, each of which is then *reconstructed* using compressive sensing algorithms to as good a representation of the original as possible, given the information in the sample. A *signature* detection algorithm is then applied to each reconstructed sample to determine how well the signature can be detected for that case. From the overall analysis of these experiments, a relationship can be established between types and degrees of degradation and the ability to detect signatures.

To demonstrate a proof of concept of the tool, we applied our software and this experimental technique to a set of sonar data with features that were difficult for a computer to detect and susceptible to noise from the instrument. We applied a range of noise values to the sonar spectra, followed by compressive sensing reconstruction and application of an automated feature detection algorithm. From this, we determined that compressive sensing has value in improving the detection of sonar features in the presence of noise, and we gained information about how the probability of detection of the feature changes as the level of noise present changes.



The full resolution figure on the right was reconstructed from the low resolution image on the left using compressive sensing.

Our research plan for FY 2012 has several components. First, we will continue to develop the software infrastructure to run the "degradation/reconstruction/signature" experiments. Next, we will develop the mathematics and associated software algorithms to analyze results of these experiments and establish formal relationships between degradation of measurements and signature detection, thus allowing use of these results in operational scenarios or system design. Finally, we will explore possible improvements in signature detection using methods that combine the compressive sensing reconstruction techniques with the signature detection algorithm into a single algorithm.

Cyber-Attack Risk Inference Model

Patrick R. Paulson, Thomas E. Carroll, Peter A. Neorr, Chitra Sivaraman

◆ This research will develop a risk-based model of a cyber attack that will provide a dynamic risk-informed framework to prioritize the proactive protection of assets and the mitigation of attacks already initiated, thus resulting in a basis for the effective use of limited security resources. We feel that this approach will improve the ability of administrators of cyber systems to prioritize their time and resources, offering improved security for both cyber systems and associated infrastructure. ◆

Dialogue with the intelligence community indicates that cyber security professionals generally assume that their systems are vulnerable to infiltration or have already been infiltrated to some degree. With limited cyber security resources, the question arises of how those resources might be most effectively allocated to prevent or mitigate the prospective consequences of infiltration. This project will provide methods to prioritize responses available to a system administrator to minimize potential consequences to an organization's mission.

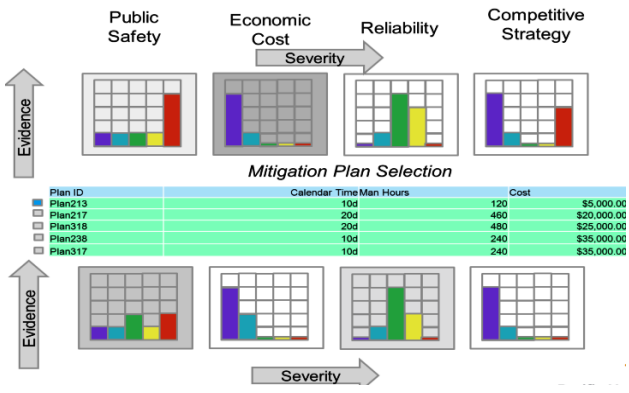
We are creating a model to provide a dynamic risk-informed framework to prioritize the proactive protection of assets and mitigation of attacks already initiated, thus resulting in a basis for the effective use of limited security resources, achieved through development of: 1) the analytic framework in which to characterize modes of cyber attack systematically, relevant protective systems, and potential consequence severities (in terms of cost impact of compromised assets and disruptions to operational continuity), 2) a repository of attack scenarios identified through analysis, elicitations, and literature review, and 3) a means of risk quantification based on probabilistic or more recently explored non-probabilistic methods.

During FY 2009, we evaluated candidate application domains, selected supervisory control and data acquisition, and defined a model framework for calculating consequences and effects of mitigations and a data model for holding application domain specific knowledge. We also elicited and constructed a prototype model in the supervisory control and data acquisition domain. In FY 2010, we developed a model exploration tool that allows domain experts to examine the state of a modeled system in terms of potential risk and assets with the greatest influence on risk. We also created a planning facility that allocates resources efficiently to address risk across multiple organizational missions. The planning is carried out in a manner that improves the risk profile across all organizational missions, rather than balancing the risk in one mission against other missions. The planning tools allow a planner to specify the levels of manpower, dollars, and calendar time to determine which actions will produce the best reduction in risk across all organizational missions. Additionally, we instantiated the domain and installation data models and created initial domain models for SCADA, business continuity, cyber security, and emergency power grid response. We also developed several software tools to facilitate model definition and instantiation.

One of our goals for 2010 was to determine if our methodology was best suited for configuration or for active monitoring of systems. Our research showed that active deployment of CARIM required little modification, and we developed API specifications to notify a deployment model of detected events to provide dynamic risk assessment.

For FY 2011, we designed a new GUI for the deployment model that communicates the evidence for risks to the organizations missions. We also reviewed literature on scalability of Bayesian networks; this resulted in a method to improve CARIM's scalability. We were able to operate CARIM against randomly generated installation which contained thousands of assets.

A major focus this year was determining the best applications of CARIM in different sectors; a detailed competitive analysis was completed and showed that CARIM has unique, desirable characteristics that are not addressed in the market place. These include the ability to assess risk to critical missions rather than cyber assets and to apply multi-criteria optimization to the problem of reducing vulnerability across multiple missions by assigning tasks to cyber security personnel and through purchase of additional systems. The problem domains of emergency response, regional and local power grids, and energy grid end-users with critical loads were examined. We determined that the initial target of reliability of cyber systems is still the most appropriate application.



The CARIM operational interface (mockup) allows operators to evidence for vulnerabilities to missions and evaluate the effect that proposed operational plans have on mission vulnerability.

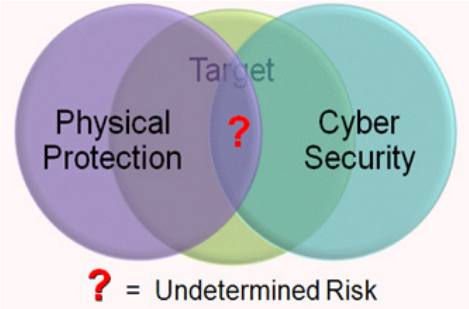
Cyber/Physical Security Vulnerability Assessment Integration

Douglas G. MacDonald, Samuel L. Clements, William J. Hutton, Scott W. Patrick, George Muller, Casey J. Perkins, Mary J. Lancaster, Edward J. Ellis

◆ This project will evaluate physical and cyber vulnerability analysis (VA) techniques and provide a strategic approach to integrate the interdependent relationships of each into a single VA capability, enabling increased identification and assessment of the overall risk during a vulnerability assessment. ◆

Existing VA processes and software tools exist and are heavily utilized in determining predicted vulnerabilities within the physical and cyber security domains. The problem is that the majority of the determinations is performed independently and interacts only on a superficial level. Both physical and cyber security domains offer solutions for the discovery of vulnerabilities, but neither method fully represents the true potential security risk to a site, facility, or asset nor comprehensively assesses the overall security posture. This project will produce subject matter experts (SMEs) that understand the potential effects each domain can have on the other, and transform the existing suite of software tools currently utilized in the physical protection world to more accurately identify and assess the risk associated with a "blended cyber/physical" attack scenario. This new methodology and software capability will allow the security analyst to determine a more accurate risk than is currently accounted for in most vulnerability assessments.

The first task in this endeavor was to bring SMEs from the cyber world and the physical world together and develop a "common language" by clarifying the various meanings of key terms shared between the two domains. With this common language and a better understanding of system level interactions, the SMEs were able to apply this to a blended system framework for analysis. They could then conceptualize how each element can be affected by neighboring elements in the overall framework.



Interactions between the physical protection elements and the cyber security domain that are not currently accounted for in many vulnerability assessments.

This year's research focused on determining how each protection element in one domain could be degraded by attacking a safeguard in the other. Understanding the component level dependencies ultimately provides a more accurate prediction of vulnerabilities associated with the composite system. PNNL and industry SMEs applied the "blended analysis" methodology to various representative scenarios in four categories: physical only attack, cyber only attack, physical enabled cyber attack, and cyber enabled physical attack. The data collected were used to refine the new VA process, improve the methodology, and design a "real world" assessment plan. A local critical infrastructure entity volunteered to host this blended physical/cyber security assessment on a proof-of-concept basis, and the lessons learned have been integrated into this effort.

Another key aspect of this new process is the ability to accurately model and quickly assess each potential pathway to the target and identify each sub-system vulnerability, and how it could affect the overall protection of the asset. A new prototype software tool was created to model each potential pathway in a given scenario, and demonstrate the degradation a cyber attack could have on the physical protection system and reveal the physical threats to an electronic communication system. This new tool is the first of its kind to model multi-directional traffic in an attack scenario, allowing the adversary to transverse areas in either direction (forward or backward). This flexibility allows the analyst to model the effect of degrading a protection element in one domain (given a successful chain of certain events), and then "back tracking" to exploit this weakened state in the other domain. This also requires analyzing every potential pathway, from off site to the target, taking into account the sub-system and component level interdependencies. The tool's output is a visual and statistical representation of each potential pathway, which is intended to highlight the elements that are commonly exploited in successful attacks. The results of this tool will help guide security investments by improving the most vulnerable paths.

FY 2012 will be used to add functionality to the prototype software tool and to populate the model's performance database with realistic safeguard performance metrics. Building probable scenarios with "real-world" data will allow the new software tool to be benchmarked against existing assessment tools, and will provide the security analyst an opportunity to visually assess the "what if" cases. For the first time, the VA process will be able to account for (and quantify) the previously undeterminable risk associated with the inability to predict component level interactions.

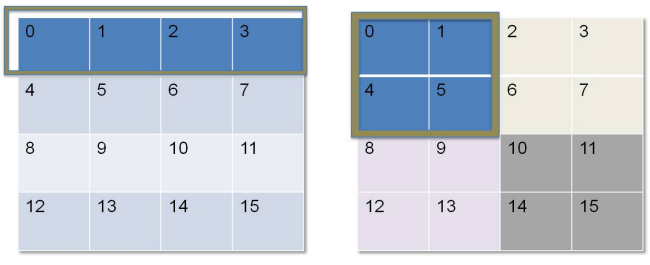
Data Decomposition/Optimizations and Dynamic Load Balancing Mechanisms for Extreme Scale Computing in the Global Arrays Toolkit

Manoj Kumar Krishnan, Bruce J. Palmer

◆ The goal of this research is to develop capabilities in the global arrays (GA) toolkit to support flexible data decomposition, communication optimization, and load balancing approaches for communication intensive applications. To address the extreme-scale computing challenges in GA applications, we will focus on developing flexible data decomposition, tackling load imbalance, and locality and communication optimization capabilities. ◆

Data decomposition is a highly effective technique used to distribute data among processors. The performance of applications can be significantly improved by selecting an appropriate data distribution. Balancing the computation load amongst the available processors is crucial to effectively exploit and scale applications on extreme scale systems. Different applications exhibit different types of load imbalance, and the appropriate solution scheme depends on the computational structure of the applications. In addition, the complexity of extreme-scale systems presents several challenges to large-scale scientific applications. To achieve scalability and performance in these systems, data decomposition, communication, and dynamic load balancing play a key role for several applications, including molecular structure and simulation calculations and subsurface modeling.

We will focus on providing the following capabilities in GA: flexible data decomposition, dynamic load balancing, and locality and communication optimization. This project will add new capabilities within the GA programming toolkit to address extreme-scale computing challenges in GA applications. We will demonstrate the effectiveness of new capabilities in the context of two important applications areas (molecular and subsurface modeling) of interest to the larger extreme-scale computing community.



Block-based data decomposition (regular, SMP-aware).

In FY 2010, we developed a limited feature flexible data distribution mechanism for GA toolkit based on the Restricted Arrays capability in the GA toolkit that allowed us to lay out data using a Hilbert curve or Morton ordering, instead of the usual column major ordering that is the default for GA. This allowed us to designed and implemented symmetric multi-processor (SMP)-aware topology distribution for better performance as the current GA model (and most PGAS models) assumes flat hierarchy for data distribution.

The performance of a topology-aware GA has been demonstrated using a GA-based ghost cell update kernel on Chinook. The topology aware ghost cell update performed 30% better than the topology oblivious kernel. The behavior of a 3D FFT algorithm was also examined to determine the benefits of different data distributions on performance of the FFT as a whole. We also have an initial design of scalable task counters to develop fine-grain scalable work stealing schemes for dynamic load balancing and have looked at mechanisms for improving nearest neighbor synchronization in STOMP's ghost cell update algorithm to improve overall scalability in STOMP at large processor counts.

In FY 2011, we have started development of a new functionality in GA called Global Pointers (GP) that will allow us to create arrays of arbitrary sized data objects. GP arrays are created in a manner similar to ordinary GAs but initially contain no data. Each process can assign the array elements that are located on that process to an arbitrary object on that process that is contained in local memory. Any other process can then obtain a copy of that object using a method analogous to the put/get operations used in ordinary GAs.

The interface for this new capability has been designed, and most of the basic functionality has been implemented. A new mechanism is included for locally allocating blocks of registered memory that can be used to create the objects that will then be stored in the GP array. This functionality allocates a segment of memory that contains a segment of memory large enough to satisfy the memory request plus a prepended segment that is invisible to the user but contains metadata on both the local and network addresses of the visible memory segment. In turn, this allows the memory to be accessed remotely from other processors using one-sided protocols. Work is currently ongoing to complete an initial implementation of the basic put/get functionality that will allow users to access blocks of data elements and copy them into local buffers. Further development work in FY 2012 will focus on adding a gather/scatter capability to the GP arrays toolkit. The GP capability will allow us to create relatively complex and arbitrary data distributions. An initial target is block sparse matrices.

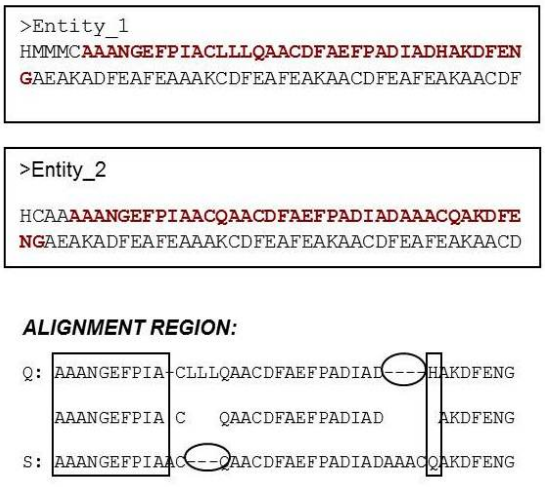
Data-Intensive Algorithms for Bioinformatics-Inspired Signal Detection

Christopher S. Oehmen, Daniel M. Best

◆ This project aims to develop a general-purpose method for discovering sequence-based signatures that can be used in solutions to cyber and network security challenges. ◆

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 exploit methodologies.

This project is directed at developing capabilities to enable the construction of a collection of solutions to challenges in cyber and network security. This method is most impactful when a sequence of events or behaviors is necessary to discriminate between true and false identifications. The root of the method is derived from bioinformatics-based techniques for discovering sequences of text that are more similar than one would expect by chance. We extend this concept, originally applied to gene and protein sequences, to arbitrary sequences of events. 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 would have significant operational impact by enabling pattern-based, data-driven identification schemes grounded in a theoretical framework to augment the current rule-based approaches to cyber security. The intent is to extend existing algorithmic and computational infrastructure so that it can be applied to a wider space of potential applications in cyber security and other domains.



Bottom: Alignment between the two highly conserved regions (bold) in the two entities above. Boxes show blocks of exact matches (left), a mismatch (right), and circles show insertions necessary to align the two sequences.

In FY 2011, this project accomplished an abstraction of the alphabet and implemented an alphabet-independent scoring matrix. We built upon prior work, where we developed a pipelined process for ingesting raw data sequences and converting them to strings of text suitable for use in bioinformatics-based analysis. One limitation of this process was that we were limited to using only characters that have biological meaning (e.g., A, C, G, and T, which represent the DNA bases or the 20 legal amino acid characters for proteins). There is no reason to expect that for arbitrary data types, these letters or alphabet sizes are sufficient. To generalize the alphabet, we developed software allowing users to specify their own alphabet, which necessitated extension of some of the underlying analysis in the BLAST source code to support alphabets of different sizes. For instance, low-complexity masking techniques (SEG and DUST) have hard-coded values in them that are optimized for use on alphabets of 20 or 4 characters, respectively. We extended the mathematical representation of these low-complexity methods to support a wider range of alphabet sizes.

A second necessary aspect for supporting arbitrary sequence analysis is the need to generalize the process of developing a scoring-matrix, a data structure that allows penalties and rewards to be assigned during the sequence alignment process and is domain-dependent. We implemented a scoring matrix generation process that relies only on the distribution of characters and an estimate of the rate of mismatches (mutations) in normal data. This allows us to build scoring matrices that are domain-specific. The scoring matrix is a starting point and can be enhanced by additional domain-specific data.

Last year, we explored methods for accelerating sequence alignment calculations using adaptive scheduling on multi-user high-performance computer systems. We envision this as a valuable capability for signature discovery when datasets are extremely large. For FY 2012, we will develop and implement new capabilities for analyzing the change of signatures over time by adding functionality for phylogenic analysis and profile-based models. We will also explore graph-based methods for expressing time-dependence of changes in higher dimensional objects represented by graphs.

Data Management, Feature Extraction and Analysis at the Extreme Scale

Brian D. Ermold, David M. Asner, David E. Cowley,
Kerstin Kleese van Dam, Michael R. Peterson

◆ Many of DOE's key science areas are not only data intensive but are also moving toward the extreme scale in terms of data needs. New scalable data intensive technologies are needed for the management, access, integration, and analysis of these unprecedented data volumes. ◆

The Belle II collaboration is an international team of physicists and engineers conducting research at the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. Currently, this collaboration is developing a new data management system that can scale from 5 petabytes of data in the year 2014 to over 250 petabytes by 2019. One of the key challenges in dealing with datasets of this size is efficiently distributing data processing across multiple systems. To accomplish this task, they are actively adopting grid infrastructures and technologies into their computing environment. Another issue is selectively identifying events of interest without the need to rescan the entire dataset continually.

The first objective of this project was to evaluate the computing infrastructure required for PNNL to interact within emerging extreme-scale data management collaborations such as the Belle II collaboration. The second objective was to examine the design criteria for data and metadata management systems to provide efficient access to events of interest in extreme-scale datasets. The project commenced with the creation of a test server that was intended for use investigating the computing infrastructure and metadata database requirements. Shortly after this was set up, the Japan earthquake hit, and the KEK facility hosting all the Belle data was operating on limited power. At this point, PNNL provided additional resources in an effort to host a subset of the data at the lab. An existing high speed data transfer node (DTN) was mounted on the test system, and over 100TB of data was transferred to PNNL. During the transfer, the Belle software stack was installed on an existing 1000 node cluster (NWICE) to create a Belle computing cluster. Rocks 5.4 was then installed on this cluster to enable multiple login nodes, making this is the first cluster at PNNL with this version of Rocks. After the creation of a security plan, the system became available to external scientists via Secure ID.

The Belle II software stack is now being installed on the Belle cluster to prepare it for GRID access. This will not only facilitate the creation of a Belle II grid site but will also provide physicists with additional data analysis tools that do not exist in the previous version of the Belle software. The next steps in creating a Belle II grid site will be to obtain a grid certificate from DOE and join the Belle II virtual organization. Once this is done, the Open Science Grid (OSG) middleware and Distributed Infrastructure with Remote Agent Control (DIRAC) server will be installed. The DIRAC server is used to unite the various grid resources including the WLCG, KEK computing center, and the OSG.

The Belle II collaboration has already chosen to use AMGA (a grid-based metadata system) for their file-level metadata system and the LCG File Catalog (LFC) for locating files within the grid network, so we focused our attention on designing an Event MetaData Catalog (EMDC) that can be used to identify the events of interest within the files themselves. Several open source databases were considered for the EMDC including hadoop/hbase/hive, Cassandra, and PostgreSQL. The first two are modeled after Google's BigTable design and are designed for large scale distributed systems. PostgreSQL is the most advanced open source RDBMS and is the backend database used by AMGA. We chose PostgreSQL for this project because it provides the speed and scalability required and will integrate nicely with the AMGA system.

Currently, the physics attributes that should be stored for the event-level metadata in the Belle II data are under discussion. This required a flexible design that allows metadata attributes to be defined as they are determined to be important. To accomplish this, the EMDC model defines metadata classes each with their own set of attributes. Additional classes can be defined as new attributes are determined to be important or as new sensors are added. The attributes for each metadata class are stored in their own table, which implements a form of horizontal partitioning and allows for sparse metadata and parallel database loads to increase performance.

Finally, in the Belle II data, each stream from an experiment would correspond to a single dataset. Further, a prototype database and API layer were developed to test our EMDC model, and preliminary results show load speeds of 5,000 events per second using two metadata classes with eight attributes. It is expected that load speeds of twice this can be achieved in a distributed system that takes advantage of the parallel nature of the design.

The Belle II experiment is expected to produce over 1 trillion events between 2014 to 2019. It is not feasible for a single database table to contain this many rows, so vertical partitioning was also needed. The EMDC model accomplishes this by subdividing events into smaller datasets.

Deception for the Defense of Cyber Systems

Thomas E. Carroll

◆ This project investigates deception and its value in defending cyber systems. We are modeling deception mechanisms using game theory and other tools from economics and applied mathematics in order to draw conclusions about the viability of deception augmenting cyber system defenses and to answer questions about the most effective types of deception and how best to deploy them in the field. ◆

Deception has a long history in warfare, the successes from which have led researchers and practitioners to use it in the defense of cyber systems. Deception creates uncertainty for attackers, as they respond by expending additional resources and taking disadvantaged courses of action. Defenders will conserve their resources, and the attackers' actions will contribute to detection. The study of deception is complex; there is no current unified theory that describes the foundations, and the current modeling techniques are insufficient to predict outcomes. One reason for this is that historically attackers witness a specific deceptive technique only once in their lifetime; another is that it is difficult to prepare for deception. However, in the context of cyber systems, effective defenses are widely deployed, giving the attackers many opportunities to experiment. This benefits us in that game theory, the study of adversarial interactions, can then be applied.

In this project, we are examining specific deceptive techniques by developing models based on game theoretic foundations. Conclusions are drawn from these models about the value of deception and how to deploy it efficiently. By applying models that combine game theory and cognitive reasoning, we are investigating the benefits of deception in protecting cyber systems. Each deception technique is being examined under various attacker capabilities and with basic learning. The outcome is to demonstrate that deception efficacy depends not only on the attacker's capability but also exposure to the technique. As an attacker becomes familiar with a specific technique, efficacy should diminish.

In FY 2010, we examined the deception technique of fake honeypots. A *honeypot* is a system whose purpose is to detect or deflect unauthorized use and access. Attackers are aware of honeypots and will rationally avoid them when possible. *Fake honeypots* take advantage of attackers' aversion by disguising normal systems as honeypots. We developed several game theoretic models that examine the interaction between network defenders that deploy fake honeypots and attackers who try to breach their networks. Solving these games, we identified pairs of strategies, one strategy for the defender and one for the attacker, and the choice of strategy pair identifies the outcomes of the games. The pair of strategies rest in equilibrium and, consequently, neither player gains by unilaterally deviating from their chosen strategy.

We began FY 2011 by examining *network address shuffling*, a concealment technique in which the one-to-one relationship between network address and system(s) changes with time. Shuffling shortens the timeframe when information gained from reconnaissance, probing, scanning, and enumerating is effective. In essence, we hoped to hide target systems in a large pool of undesirable systems. We developed probabilistic urn models to investigate the relation between the number of probes transmitted by the attacker and the chance she successfully identifies valuable targets, and the relation between shuffle frequency and cost to the defender. We have conclusively shown that the attacker's success rate decreases with increasing shuffle frequency. Unfortunately, high shuffle frequency incurs significant cost in terms of dropped network connections. Investigating the derivatives of both functions, we observed that less frequent shuffling meaningfully disrupts the reconnaissance process, while costing little to the defender. We these points in mind, shuffling defenses work best against adversaries who are scouting for targets of opportunities, and not having specific targets as objectives.

We also reevaluated our previous models under a *games of unawareness* framework. It is a game structure that models and solves strategic situations where players' reasoning is limited. The limitation arises because players are only aware of some aspects of the situation at hand or because players realize that other players' perception is limited. Both aspects are important for modeling deception in cyber space. Using the framework for fake honeypots allowed for richer detail to be incorporated into the game and allowed us to draw more specific conclusions. We concluded that the framework is a better fit for modeling deception, especially in cyber space where the adversaries are fully aware of the types of deception mechanisms that are deployed.

Finally, we performed an overview of the models and have drawn several conclusions. Single deception measures are unlikely to impede significantly the advancements of attackers. Attackers will learn about effective counter deception measures and will parlay the effects of these single measures. Thus, it is the dynamic management of several deception mechanisms that provides the greatest advantage of deterring and impeding attackers. Deception measures should be coordinated and inform other deception elements.

Developing Functionality and Performance Enhancements to the Global Array Toolkit

Bruce J. Palmer, Christopher J. Mundy, Mark L. Stewart, David R. Rector, Haluk Resat, William A. Perkins, Marshall C. Richmond, Barry Lee

◆ We are focused on determining what performance and functionality bottlenecks need to be addressed in global arrays (GA) to support applications that are expected to run on exascale platforms. Our project will help implement proposed solutions in target applications and evaluate their effectiveness. ◆

Global arrays is the premier data-centric programming model that was developed in conjunction with NWChem at PNNL. It has been used on most of the large-scale supercomputers deployed to date and is under active development at PNNL. GA's approach is focused on providing simple one-sided access to arrays of data that are globally visible from any process in the system. Though GA has been very successful for the applications that use it, the application base itself is still relatively small. Existing applications include PNNL's NWChem Chemistry code, the STOMP subsurface code, bioinformatics (Scalablast), and conventional computational fluid dynamics (TETHYS). This limited application base is a concern in that further development of GA would benefit from a broader range of requirements. Thus, this project incorporates GAs into several applications representing a diverse group of computing problems with the goal of using these implementations to understand the scaling behavior of GA in different scenarios.

Target areas in this project include sparse matrix multiplications, continuum reactions, and discrete particle tracking combined with unstructured continuum fluid flow solvers, large-scale semi-empirical electronic calculations, and lattice Boltzmann simulations of continuum flow using structured grids. These problems will help us to define a new functionality needed by application developers to incorporate GA into their codes. In FY 2011, progress was made in all four application areas.

Sparse Matrix Multiplication. A code has been developed that implements a sparse matrix-vector multiplication using the GA library and compares it with a comparable operation using the PETSc solver library. The PETSc implementation is currently faster than GA but we have had difficulty running it on larger problems, which the GA implementation can run without difficulty. We are in the process of modifying the PETSc portion of the code so that it will work with very large matrices. This will bring a complete scaling comparison between GA and PETSc and allow us to analyze the GA code so we can improve overall performance.

Semi-Empirical Electronic Structure Code. Coulomb interaction contribution to the Kohn-Sham matrix in the CP2K electronic structure code converted from its original replicated-data implementation using MPI to a fully distributed algorithm using GA. Algorithmic correctness was verified, but expected scaling behavior has not been achieved. The GA implementation uses fully distributed data and is expected to scale for large problem sizes and high processor counts, while the replicated version is expected to consume a larger fraction of computer time and memory resources as problem size increases. The GA implementation is currently being analyzed to determine the cause of poor scaling.

Reactive Chemistry and Particle Tracking. Chemical reactions and some particle tracking capability have been incorporated into the TETHYS continuum fluid dynamics code with the goal of eventually simulating growth in a bacterial micromodel. This model combines continuum modeling of reactions using standard reaction-diffusion equations with reactions associated with discrete particles modeled using Lagrangian methods.

Lattice Boltzmann Algorithm. The PARAFLOW lattice Boltzmann simulation code has been converted to use GA for the ghost cell updates that are a core part of the algorithm. Comparison of the MPI and GA versions of the code indicate that the GA implementation provides comparable performance to MPI. The lattice Boltzmann application is a test case for studying new mechanisms for guaranteeing data consistency in GA without using a global barrier. The iterative aspect of this particular lattice Boltzmann algorithm also provides an opportunity to look at load balancing as well.

In FY 2012, we expect to complete several tasks. First, we will modify the sparse matrix code so that large problems can be run using the GA-based and PETSc kernels and analyze GA performance to determine how to match message-passing behavior for large problems. We will complete a version of the Kohn-Sham electrostatic calculation that scales to large processor counts and large problems sizes in memory and performance. We will also incorporate the PT6 particle tracking code into TETHYS and implement a bacterial micromodel that couples fluid flow and transport with bacterial growth in porous media. After load imbalance in the kinetic Lattice Boltzmann model with a solution implemented based on global counters, we will investigate a looser data consistency models for ghost cell updates. Finally, we will implement the proposed Global Pointer Array capability, including basic put/get and gather/scatter functionality.

Development of Exascale Algorithms for Molecular Modeling

Karol Kowalski, Eric J. Bylaska, Marat Valiev

◆ Our main purpose is to develop new modeling tools that can be effectively used on next generation computer architectures. In particular, we will significantly advance time and spatial scales of multiscale simulation methods and excited state methodologies. ◆

A wide range of molecular processes require highly diversified methodologies to describe systems characterized by different time and spatial scales. In a vast majority of situations, this problem entails a need for having multiscale methods built upon fundamental solvers whose scalability and accuracy define the final performance of combined approaches. Given the dramatic increases in computer technology over the last decade, it is expected that exascale capability will lead to a significant shift in the system size and time scales. The progress in enhancing parallel performance of multiscale methodologies rests upon concomitant, balanced development of all constituent parts of a given multiscale approach. In the proposed research, which aims at the achieving scalability across 10^6 or more processors, this translates into designing novel upscale spatial and time methods, including automated, self consistent algorithms for securing new quality of inter atomic classical potentials (as well as its extensions to excited state simulations) and development of efficient multilevel time solvers in order to push the time limits for molecular simulations.

The main objective of our research is to advance significantly the computational capability of the multiscale formalisms in order to reach the exascale or near-exascale performance. In particular, we are pushing the envelope for the spatial and time scales characterizing proposed multiscale simulation methods and develop peta/exascale tailored theories and codes for excited-state methodologies defining the computational core for quantum region. We also propose to build the link between *ab-initio* and molecular dynamic modules in order to achieve an unprecedented level of accuracy. The use of high level peta-scale coupled-cluster methods in the development of reliable MS/MP formalisms may serve as an excellent example. In this project, we clearly identify computational bottlenecks that can seriously affect the overall performance of the proposed algorithms. For the purpose of resolving these problems we envision a close collaboration with several computational science projects. As an outcome of this, we expect significant improvements in several key computational kernels.

During FY 2009, we made significant progress with several project tasks. A new coupled cluster excited state, non-iterative methodology based on the reduced iterative core was developed. In addition, a new parallel in time algorithm was implemented and tested on several benchmark systems, and novel ground state coupled channel formalism was fully integrated with multiscale, multi-physics formalism. Preliminary tests clearly showed the scalability of newly developed ab initio codes across the 6144 excited state coupled cluster methods, as well as the 20,000 hybrid density functional theory/molecular modeling approach central processing units. The reported parallel performance was demonstrated in contemporary excited state calculations for fused porphyrin dimer and hybrid density functional theory/molecular modeling approach calculations for 80 atom cell of hematite. Substantial improvements in speed, memory management, and communication pattern were achieved in the first year. Six papers reporting on this research were either accepted or submitted in FY 2009.

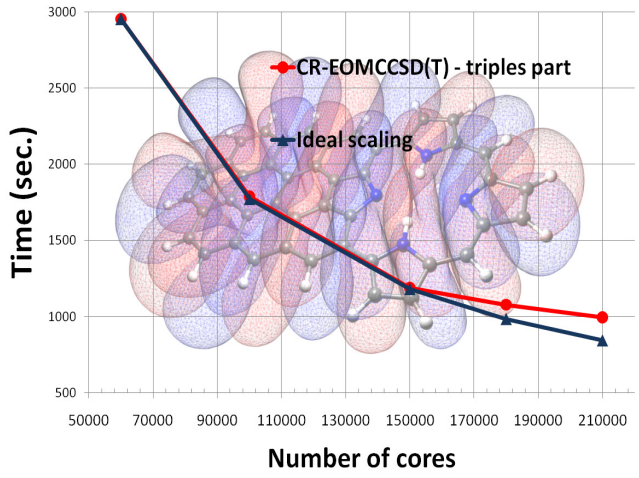
For FY 2010, we again made good progress in several key areas of this project, our research, and results. First, we initiated the development of scalable GPGPU-based implementations of the CCSD(T) and regularized CCSD(T) approaches. Specifically, the scalability of the CR-EOMCCSD(T) approach was demonstrated across 34,008 cores. All tests were performed on the Franklin Cray XT4 computer at NERSC, and the CR-EOMCCSD(T) and active-space CR-EOMCCSD(T) approaches were shown to be applicable in calculations for excitation energies of large molecular systems (942 basis set functions and 270 correlated electrons). We demonstrated that the errors in calculated excitation energies can be reduced to within 0.1 eV with respect to the experimental data.

For task scheduling during FY 2010, we implemented new algorithms for the iterative CCSD and EOMCCSD methods. We demonstrated that grouping CCSD/EOMCCSD procedures into layers collecting independent routines increases size of task pool, reduces the impact of load imbalance, and allows the use of larger tile sizes, which is essential for effective utilization of the GPU-based accelerators. In addition, we enabled the integration of newly developed high-order methods with MS/MP methods, which enabled us to perform calculations for molecular systems in solution or for surface localized states in materials. A new framework for task and data management in MS/MP calculations was implemented and applied to the optimization of large molecular structures. Further, we implemented a new parallel algorithm for hybrid DFT (incomplete butterfly), which reduced communication costs by half. A stand-alone AIMD program was converted to CUDA, and a stand-alone MPI/C++ code was being developed as well as converted to

three different platforms. The implementation and testing of global array groups in NWChem is in progress using the python interface. Finally, we implemented a general two-level parareal multiscale model using the task level parallelization python code in NWChem. For this year, seven papers reporting on project progress were either published or submitted.

In FY 2011, several major goals were achieved. First, the scalability of the most computationally intensive part of the CR-EOMCCSD(T) methods has been demonstrated across 210,000 cores on Cray XT5 computer at Oak Ridge National Laboratory. It was also shown that from 60,000 to 210,000 cores our code can be executed with 84% parallel efficiency. Our tests also helped us to eliminate local memory bottleneck of the (T) part of the CR-EOMCCSD(T) approach. By partitioning of high-dimensional tensors in the non-iterative part we can fully control the local memory usage and make our codes portable to future architectures characterized by small memory per processor. This partitioning introduces yet another level of parallelism, which can be fully exploited in our implementations. Similar changes have been implemented in the active-space variants of the EOMCC formalisms, which by reducing the cost to $N_{act}^{5}N^{2}$ (N and N_{act} designate the total number of orbitals and the number of active orbitals, respectively) make the high-precision calculations possible for large molecular systems.

The development of new parallel algorithm for hybrid DFT (incomplete butterfly) reduced communication costs by 50%. The scalability of the hybrid DFT code has been demonstrated across 94,000 cores on Hopper Cray XT6 architecture at NERSC. This breakthrough is of special importance for the parareal algorithms developed by Dr. Bylaska. We also developed parallel in time (parareal) quasi-Newton algorithms that avoid the need for a preconditioner (coarse solver). For non-trivial molecular dynamics simulations, these algorithms have been able to improve the time to solution by a factor of 10 without the utilization of preconditioners. The implementation of the parareal algorithms is based on the task level parallelization in NWChem. The implemented two-level parareal multiscale model can utilize any module of NWChem as a coarse and fine grain propagators. In test calculations, HF and CCSD methods have been used as a coarse ($G_{\Delta T}$) and fine ($F_{\delta t}$) integrators. We also implemented a CUDA Car-Parrinello program, where a factor of 10 speedup was obtained. For FY 2011, we published the first paper reporting our GPU implementation of the CCSD(T)-type approaches. New dimension flattening and three-state pipelining algorithms enabled us to achieve almost 9-fold speedup of the code. We have also achieved almost linear scalability of the (T) part as a function of CPU and GPU cores used in calculations. A paper based on our work has been accepted to the Supercomputing 2011 Conference.



Scalability of the triples part of the CR-EOMCCSD(T) approach for the FBP-f-coronene system in the AVTZ basis set. Timings were determined from calculations on the Jaguar Cray XT5 computer system at NCCS.

Ultimately, our project will potentially have a long-standing effect on the routine calculation performed on the next generation of computers. We anticipate a significant shift in both system size and accuracy level characterizing exascale molecular simulations in many research fields. The achieved progress has made it possible to treat systems accurately with 200-400 correlated electrons routinely. Recently, the new algorithms have been used in cutting-edge studies of spectroscopic properties of polyacenes and functionalized forms of the porphyrines, which are the basic building blocks of the many light harvesting systems. The ability to design novel light harvesting complexes rationally and accurately is a key component of our work. Our high-level methods have also been integrated with the Embedded Cluster method, which enabled us to describe the localized excited states in solid state chemistry/physics. In recent studies, high-level methods were employed to predict the changes in the spectrum caused by the presence of dopands on the TiO_2 surface. The obtained results properly predicted the changes in the spectrum and verified the role of the N^{3-} states on the observed spectrum of N-doped TiO_2 rutile as suggested by experimental findings.

The outcomes of this project are computational chemistry algorithms that have been published in the scientific literature, including scalable, excited state approaches for exascale molecular simulations, the efficient interface between ab initio theories and multiscale, multiphysics simulation module, and the exascale parallel in time algorithms (or parareal algorithms) integrated with terascale ab initio molecular dynamics and the terascale molecular dynamics programs.

Development of Parallel Multi-Reference Coupled Cluster Capabilities

Hubertus J.J. van Dam, Karol Kowalski, Jiri Brabec, Kurt R. Glaesemann

◆ This project will bring out the extreme levels of scalability that are in principle available in multi-reference coupled cluster methods. The resulting implementations will be able to address important problems in areas such as transition metal catalysis and chemically reactive potential energy surfaces, for which multi-reference methods are essential. ◆

Single-reference coupled cluster methods have proven to be scientifically useful for describing correlation effects in electronic structure theory. In addition, previous projects have demonstrated that these methods can be implemented in a highly scalable way. However, the single-reference methods breakdown if the chemical system exhibits near-degenerate electronic states. In those cases, there is essentially no single electronic configuration that stands out as a suitable candidate for the reference configuration. In such a situation, the only solution is to select a set of dominant configurations and use all of them as reference configurations. This is the basis of all multi-reference coupled cluster methods.

In practice, a number of multi-reference approaches have been developed following different philosophies in addressing the multi-reference problem and emphasizing different characteristics. These approaches have shown the high value of multi-reference methods for challenging problems. A major limitation of the current implementations of multi-reference coupled cluster methods is that they have not been designed for scalability instead they have been focused on the proof of concept aspects of the theory. Interestingly, the multi-reference methods are very promising candidates for parallelization. This follows from the structure of the equations that allow for two levels of parallelism. One level of parallelism comes from the equations associated with a single reference configuration, which we have already shown can be made to scale well. The second level of parallelism comes from the fact that all the reference configurations can be treated concurrently.

The objective of this project is to express the parallelism inherent in the multi-reference methods for a variety of methods. Our research involves a thorough analysis of the coupling terms between the equations for the different reference configurations as this will dictate how the parallelism can be expressed. Also, the importance of couplings of different types will be considered in relation to their impact on the achievable parallelism. Ultimately, this project will deliver extremely scalable and scientifically versatile capabilities for studying a comprehensive set of chemical systems.

A mid-year FY 2011 start, this project concentrated on the Brillouin-Wigner multi-reference coupled cluster method. This method uses particularly simple coupling terms but already has all the basic infrastructure needed for any multi-reference coupled cluster approach. We implemented improvements to handling integral files and the use of task pools, and we demonstrated the basic parallelism this method can achieve. We found that even at this level, the code scales to at least an order of magnitude more processors than previously reported in the literature. In addition, we found that triples corrections are important for achieving highly accurate results, even in the multi-reference case. The results from this study have been submitted for publication. Also, an analysis of perturbative correction terms has been performed focusing on both accuracy and achievable scalability. This study prepared the ground for the parallelization of perturbative triples terms, the outcomes of which have been published. In addition, we have been invited to talk about the project at an international conference.

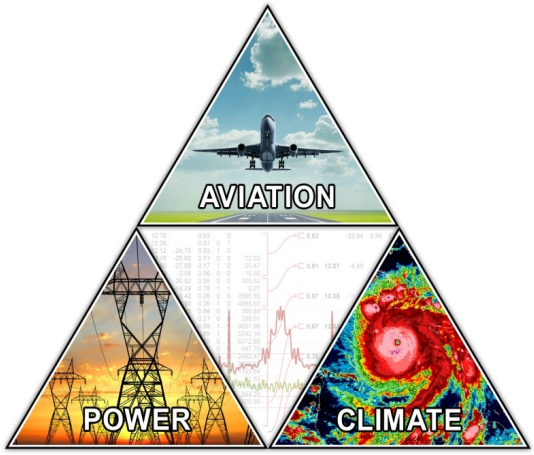
In FY 2012, we will focus on three main areas. The first development will be to change the current code from solving the equations for the different references one after another to solving these equations concurrently. This way, we will be able to access the second level of parallelism mentioned earlier. The second development addresses the parallelization of the perturbative triple contributions. This addition has two important benefits. From the scientific perspective, we know that the triples contributions are essential to achieve the high levels of accuracy that are needed to answer important questions for the kinds of systems the coupled cluster methods were designed for. From the computational perspective, the triples corrections have the beneficial property that they improve the scalability of the code significantly. In combination with the parallelization over references, this implementation should impressively boost the scalability overall. The third development will be to look at parallelizing the next level of multi-reference method. The Brillouin-Wigner multi-reference coupled cluster suffers from a loss of size-extensivity. This is a well-known artifact of significance as coupled cluster theory was formulated exactly for its exact size-extensivity. However, a number of remedies have been proposed to eliminate this artifact. We will implement highly scalable variants of these corrections.

Domain-Independent Feature Vector for Time Varying Multivariate Data and Signature Characterization

Thomas A. Ferryman, Brett G. Amidan, Connor J. Flynn, Jeffery E. Dagle

◆ The aim of this research is to develop a tool to monitor very large complex systems in different domains, such as the electric power grid or climate data, to reveal typical and atypical events and enable alerts about system behavior in real time. In these areas, the situational awareness and real-time alerts could enable quick response and mitigation to undesirable conditions. ◆

Complex systems are ubiquitous throughout society. We examined data from complex systems in aviation, the electric power grid, and climate. Situation awareness is essential to keeping these systems up, operational, and safe. Monitoring the systems for deviations from normal operation is also critical. The goal of this project is to investigate the development of comprehensive feature vectors that use a domain-independent methodology and capture the essence and nuance of underlying phenomena in an easily analyzable structure to enable identification of typical patterns and atypical events. The project has a second goal to demonstrate this capability on multiple domains. Once we demonstrate on multiple domains, we will gain insight about generalizing the tool and applying it to other domains to determine which domain characteristics are key to using these techniques effectively.



Large complex aviation, electric power grid, and climate data sets were used to develop comprehensive feature vectors that enable situational awareness of those systems and real-time alerts to atypical events.

This project is advancing PNNL capabilities, using the following different data sets:

- Aviation data collected via on-board instrumentation that captures anywhere 100 to 3000 variables at 1-sec intervals for the duration of thousands of flights.
- Air traffic control data associated with thousands of aircraft during their approach to a single airport.
- Electric power grid data collected at approximately 100 locations at 30 Hz rate for 24 hrs/day over 30 days. The data consisted of several hundred different variables.
- Electric power grid data associated with thousands of locations that were collected around the clock at 5-min intervals for 15 months (hundreds of variables).

In each case, typical patterns and atypical events were identified. The information was shared with domain experts and reported to provide new, useful insight to increase situational awareness of the system's behavior and identify interesting, atypical events. These demonstrations represented an important and new kind of situational awareness and alerting capability.

Our key goals included discovering the data types to be effectively analyzed by this approach and how we can make it more generalizable and applicable to additional domains. Our objective was to demonstrate the approach on two different data sets and gain knowledge on the above research questions. This objective included demonstrating our tool's ability to create comprehensive feature vectors and identify typical patterns and atypical events.

We acquired copies of two data sets from the Atmospheric Radiation Measurement Program: Radiatively Important Parameters Best Estimate (RIPBE) and Climate Modeling Best Estimate (CMBE). We proceeded to apply the methodology, and we identified problems and created solutions as we progressed. For each data set, we created comprehensive feature vectors to identify typical patterns and atypical events.

The two most important results of the year's research were first, demonstrating the use of the tool on two additional data sets and in different domain. This activity underscores domain independence of the methodology. Second, it was vital to create a method to handle distinctly different data collections rates in a joint analysis (RIPBE was collected every minute, and CMBE every hour).

For the first time, these techniques enabled a comprehensive analysis of several years of information for each data set to identify typical patterns, report the date/time of those weather patterns, and identify characteristics of those weather patterns.

Enabling Hypothesis Driven Research and Discovery in Extreme Data

Kerstin Kleese van Dam

◆ The goal of this project is to discover the significant limiting factors preventing today's scientists from making better use of the existing archives by using a wider range of investigative methodologies. We will explore strategies from the aspect of several different types of sciences to overcome previously identified limiting factors and develop a prototype research environment. ◆

Advances in experimental and computational technologies have led to an exponential increase in scientific data volumes and their complexity. This data has resulted in the creation of a fast growing number of data collections, at times of extreme size. Unlocking the inherent potential in these data collections by enabling scientists to carry out hypothesis-driven research and discovery through effectively synthesizing and probing data as a community and across boundaries will provide extraordinary scientific advantages. However, to achieve the translation of the collected data into exploitable knowledge requires a paradigm shift both in terms of tools and human behavior. The advent of extreme data has led to the development of hypothesis-neutral data mining and social data analysis as a means to interact with the data. A new generation of tools, taking into account the human behavior, could play a pivotal role in enabling the necessary paradigm shift to support hypothesis-driven scientific research and discovery.

Studies show that researchers will assign and display human emotions toward any technology with which they interact; therefore, behavioral and social concepts that govern human-to-human interaction may partially govern researcher interactions with technology and digital information. Therefore, any new user environment must account for common practices in the research environment that are required to build necessary trust in data (and/or creator), its handling, and analysis. Additional research studied successful strategies in software environments to stimulate desired behavior, such as collaboration and data reuse.

In this project, our goal is to discover the significant limiting factors that are preventing today's scientists from making better use of the existing archives by using a wider range of investigative methodologies. We commenced exploring strategies from behavioral science, cognitive psychology, business sciences, and information technology that will enable us to overcome the previously identified limiting factors. By the end of this project, we will develop a prototype research environment that will enable greater knowledge from data collections by researchers. We will establish quantitatively and qualitatively the boundaries to exploiting extreme data collections by the communities they serve, and we will develop strategies to overcome these boundaries based on methodologies from the aspect of various difference sciences.

In FY 2010, the project broadly evaluated the extreme-scale data intensive science requirements of both experimental and observational facilities and users with a more detailed evaluation of the needs of a variety science groups working in PNNL's major focus areas from systems biology and chemical imaging to atmospheric science and high energy physics. Based on this requirements analysis, an initial architecture concept was developed. As part of the work, we additionally identified a key gap in PNNL's provision for extreme-scale data: a data transfer node that would allow offering large-scale PNNL data sets to its customer base as well as enabling PNNL scientists to access their own (and other people's) scientific data elsewhere.

During FY 2011, the project team was extended, and we worked on developing an initial prototype research environment that supports the collaborative, hypothesis-driven research in extreme-scale data. Involvement with other research in chemical imaging and BELLE II provided access to extreme-scale data repositories and additional user groups. In collaboration with Valerio Pascucci (University of Utah), the requirements for a visual data exploration and analysis environment were explored as part of the collaborative discovery environment CAT. Utah will complete an initial analysis of the data structures and architecture design for two pilot projects throughout the year. This project work has led to four invited talks, a white paper, and three forthcoming book chapters.

Enabling the Meaningful Exploitation of Integrated Regional Earth Systems Data

Kerstin Kleese van Dam, Yan Liu, Carina S. Lansing, Eric G. Stephan, Maria Vlachopoulou

◆ This project will develop a flexible coupling software framework for multi-scale, multi-disciplinary integrated regional earth systems simulation models as well as design and implement a supporting research infrastructure to enable the collaborative development and exercise (including uncertainty characterization) of the modeling framework and necessary collaborative analysis and exploitation of results. ◆

The fundamental goal of the Integrated Regional Earth System Model (iRESM) is to develop a modeling framework that enables the critical analyses of the tradeoffs and consequences of decision and policy making on the background of integrated human and environmental systems, combining a wide range of different scientific and economic processes. While initially focusing on the modeling interactions of climate, socio-economic, crop and energy systems, further inclusion of other science domains such as biogeochemistry, subsurface flow and medicine are envisaged for the future. Coupling models from such different disciplines and backgrounds presents a range of key scientific, computational and data challenges:

- Consolidating and integrating overlapping processes consistently across models
- Define scientific relevant exchanges and feedback between models
- Significant variability in spatial and temporal scales
- Different simulation models, programming languages, implementation approaches, and computational requirements
- Different data formats and variable names
- Differences in data structure and representation as well as semantic differences between the different scientific domains involved.

Thus, what has to be overcome are significant scientific, technical, syntactic, semantic, and communication challenges to enable the successful integrated model framework development, including model coupling, evaluation, and numerical experiments to address the relevant scientific questions. To facilitate information exchange, evaluation, and usage of results by the project team and stakeholder community, a rigorous data model needed to be designed that integrates the data, information, and knowledge provided by each into a form in which different aspects can be flexibly represented to the appropriate user communities.

In FY 2011, our project designed a decentralized knowledge model that can leverage the existing community specific standards and vocabulary for data and metadata (such as NetCDF CF), which are then integrated via ontologies that create "cross walks" between the different disciplines where overlaps exist. They also help to define groupings of subject areas such as "reservoir modeling," helping to classify overlapping areas between the derived data models, distinct areas specific to particular data models, or new areas that can only be defined by combining data models.

In May, the efforts of two projects were integrated under the leadership of one to provide an integrated approach to collaborative model coupling and evaluation, numerical experiments, and modeling framework result evaluation. The joined projects developed a flexible, hybrid coupling approach that facilitates close coupling of models where possible and a loose coupling where required. The employed MeDICi workflow system for loose coupling helps bridge differences in model implementation approaches, runtime, computing platforms and data representation. It also provides flexibility to include and remove models, as required. Initial implementation work on the loose model coupling was started in September, building on one of the project's prior work.

Given the complexity of the framework development challenges, it will be necessary to provide a supporting research infrastructure that will offer a collaborative platform to access versioned data, model, and tools, discuss and document scientific and technical model coupling issues, and support model and framework evaluation over time from planning to execution and evaluation. More importantly, the infrastructure will be required to carry out scientific studies with the integrated modeling framework, allowing the concentrated documentation of discussions, decisions, experiments, results and analysis throughout the process as well as providing access to data, models, workflows, and tools to support experimental planning, execution, analysis, and evaluation. We designed an initial infrastructure, and implementation has started on core components, building on some prior work in other domains.

In FY 2012, we will implement the first prototype of both the hybrid model coupling approach and the supporting iRESM infrastructure to support the model evaluation efforts and numerical experiments.

Exploring Architectures Suitable for Scientific Applications at Exascale Levels

Oreste Villa, Andres Marquez

◆ The aim of this project is to provide guidance to PNNL domain scientists on the refactoring and design of algorithms suitable for future exascale platforms. Current and future DOE applications will benefit from the ability to run faster and more accurately on large-scale machines. ◆

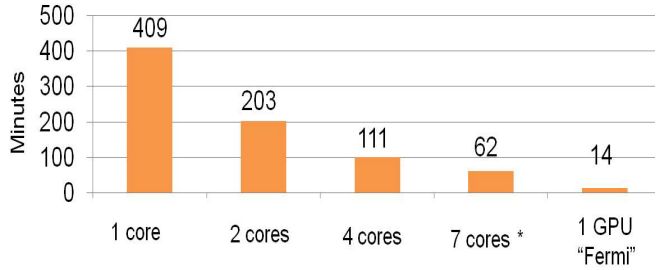
Given recent computer hardware design, it is likely that a future exascale system would contain hybrid processors composed of hundreds of cores and/or special purpose hardware accelerators. This project focuses on the evaluation of novel architectures that, in large-scale system configurations, can potentially achieve performance at exascale levels (1 billion billions of floating point operations [FLOPS]/sec). A recent promising trend in computer architecture design is stream processing, an execution paradigm that allows some applications to exploit parallel processing. Such applications can use multiple computational units (such as floating point) without explicitly managing allocation and/or communicating among units. One of the most common forms of stream computing is in graphic processing units (GPUs). Current GPUs are highly parallel multicore, multithreaded accelerators capable of performing general purpose computations. As accelerators, they must be interconnected through a central processing unit (CPU)-based host system. This project addresses the computational challenges involved in molecular simulations and subsurface flow and transport applications at PNNL.

In FY 2009, we investigated the use of GPUs in the context of molecular dynamic simulations, a computationally intensive method used to study the time evolution of a system of atoms using Newton's classical equations of motion. We implemented a functional and complete GPU enabled molecular dynamic simulator capable of calculating bonded and non-bonded forces between atoms of a periodic system. As reference, we implemented a multithreaded non-bonded force calculation on conventional CPUs to test performance and correctness of the GPU counterpart. On double precision, the GPU code outperformed the CPU base code 15 times with cutoff and 10 times without cutoff.

During FY 2010, we investigated the use of the NVIDIA GPU "Fermi," which is used as base for the NVIDIA TESLA C20 family. This processor is composed of up to 512 cores running at 1.15 GHz and is able to achieve a theoretical peak performance of about 1 TFLOPS in single precision and about 500 GFLOPS in double precision. A cluster of GPUs the same size as PNNL's Chinook supercomputer (2130 nodes) would be able to achieve a theoretical peak performance of about 10 PFLOPS in single precision and 5 PFLOPS in double precision. As reference, Chinook has a peak performance of about 0.2 PFLOPS. NVIDIA GPUs are programmed using Compute Unified Device Architecture (CUDA) software architecture for issuing and managing computations on GPUs.

In FY 2011, we investigated the use of the Nvidia "Fermi" GPUs in the PNNL NWChem software suite specifically for the CCSD methods, which are used to calculate the approximate solution of the Schrödinger equation. They are successfully used to understand fundamental optical processes in solar cells, photosynthesis, and other optically active materials. We applied our accelerated code to the CCSD calculation of the Green fluorescent protein with 284 and 476 basis functions. We observed the completion times on a 16 nodes GPU accelerated cluster. Each node is composed of two quad-cores Intel Nehalem 2.66 GHz processors and a Tesla C2050 "Fermi" GPU. On conventional cluster, the CCSD portion of the calculation is responsible for greater than 70 percent of the total computation time. A single GPU outperforms two quad-cores Intel Nehalem 2.66 GHz processors by a factor of 4.

Also in FY 2011, we focused our efforts on another PNNL key application, namely STOMP. STOMP is a computer model simulating subsurface flow and transport specifically designed to provide multidimensional analysis capabilities for modeling subsurface flow and transport phenomena. In this context, we developed a task based library that seamlessly utilizes CPUs and GPUs for the computation of STOMP chemistry reactions. The library uses optimized batching schemes to transfer data In/Out the GPU memory while overlapping transfers with computation. The overall benefit of this approach gives a speedup of ~18 respects with a single CPU core by using 2 GPUs while computing the reactions for 32 species over 1 million grid cells.



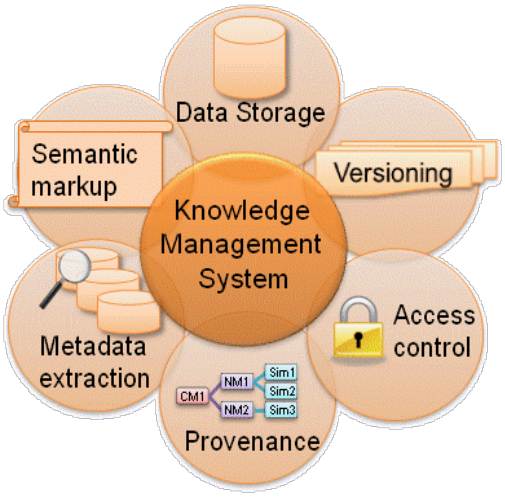
Performance of the CCSD(T) calculation on a 16 nodes cluster.
** 1 core is used by the communication engine.*

Geological Sequestration Software Suite Core Architecture and Simulation Framework

Ian Gorton

◆ Our geological sequestration software suite (GS^3) is a set of tools integrated through a software framework that supports the modeling process used to evaluate and monitor carbon dioxide sequestration sites. ◆

Geologic sequestration is a technology currently being developed to mitigate global warming through the long-term storage of greenhouse gases. Finding suitable subsurface (underground) sites for sequestration of greenhouse gasses requires performing extensive studies that include modeling the site geology and the processes that determine the fate and transport of injected gasses. Subsurface modeling is an iterative process that can often take months or even years to complete and is continually revisited as new information is gathered. In addition, work is performed not by a single scientist but by interdisciplinary teams comprised of geologists, hydrologists, engineers, geochemists, and computational scientists who are unlikely to be co-located.



Components of the GS^3 platform.

In FY 2009, we designed and built a prototype version of GS^3 and demonstrated it to various groups involved in carbon sequestration. The software adopts a novel layered architecture that enables it to be highly customizable for generic modeling and simulation environments. Based on our experiences in prototype validation, we found that the GS^3 environment is an excellent match to a scientific user base in terms of usability. We have worked extensively with geo-scientists to understand the modeling and simulation process for carbon sequestration.

For FYs 2010 and 2011, we focused on how modelers utilize a range of data throughout the modeling process. Important data types include the following:

- site data measured from well logs and experiments used to build geological models of the subsurface
- model input data that maps the geological models to a numerical grid so that it can be simulated
- simulator output data that is produced by numerical simulators such as STOMP.

Crucially, assessing the significance of simulated outputs requires detailed assessment of the simulator inputs and how they are derived. As modelers cannot "see" underground, various parameters must be estimated and a number of different input models constructed to assess the effects of these estimates. This makes it highly challenging to manage effectively the large volumes of data associated with modeling a given sequestration site.

For the reasons provided above, we created GS^3 as a core knowledge management system for carbon sequestration. More specifically in FY 2011, we worked extensively with geo-scientists both within and external to PNNL to design, build, and deploy the first version of GS^3 for use in sequestration projects. Our initial version of GS^3 is based on a number of integrated software components, as depicted in the figure.

The major components that together comprise the GS^3 knowledge management system that we designed, deployed, and upgraded throughout the past fiscal year are detailed below.

Data Storage: GS^3 includes a data repository for storing the heterogeneous data files associated with a modeling project.

Versioning: GS^3 enables modelers to create and manage model versions and associate the input and output data with a particular model version.

Semantic Markup: GS^3 contains a data ingest pipeline that can be used to markup text files in various formats with terms that are of interest to modelers. Once marked up, these documents can be searched using the GS^3 user interface.

Metadata Extraction: GS^3 ingest pipelines also read structured data formats such as well logs and extract metadata from these, for example, to show the geographical location of a well on a Google Maps interface in GS^3.

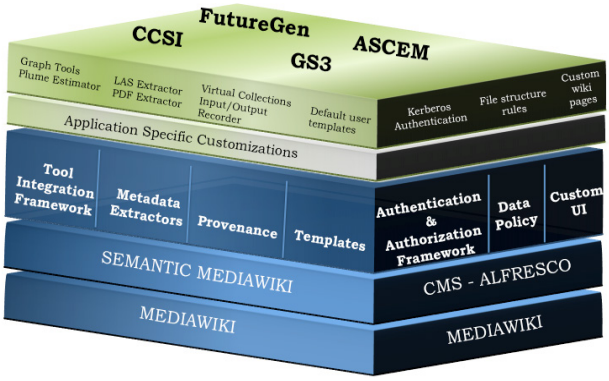
Over the year, we modified the core GS^3 design to make it possible to easily configure the tools for different deployment needs. This resulted in the core technology behind GS^3 being packaged as a reusable, flexible software platform for modeling and simulation that we named *Velo*. Velo is being applied to climate and subsurface modeling efforts.

Geological Sequestration Software Suite Framework

Ian Gorton

◆ We will design, develop, and deploy a software framework with the following capabilities that are integral to effectively evaluating and modeling potential target sites for carbon sequestration. ◆

Advanced multiphase flow and transport modeling codes coupling physical, mechanical, chemical, and biological processes are expected to play a crucial role in understanding and evaluating the feasibility and long-term effects of sequestering CO_2 in large-scale deep geologic reservoirs. However, the process of managing and interpreting raw data, building the conceptual model of the subsurface domain, and transforming/scaling into the numerical model for evaluation by these types of simulation codes is a tremendous challenge even for experienced modelers. The number of data sets and number of tools that can be applied under different conditions is extensive and difficult to manage. The process may also involve the development and evaluation of several conceptual and numerical models, leading to tens to thousands of simulations run for a single site. Organizing, managing, and tracking data at each stage are critical to the integrity, verifiability, and repeatability of the analysis yet is ad hoc, time-consuming, and error prone.



Velo architecture.

In this project, we will design and create novel provenance capture and analysis, and tool integration frameworks for carbon sequestration modeling. These capabilities will advance the state of modeling practices by providing the ability to track the data and assumptions in a given model, and make available a broad toolset for modelers to contribute to and exploit. To deploy these capabilities for modelers, we will integrate them with the Geological Sequestration Software Suite (GS^3) and demonstrate their capabilities in support of uncertainty quantification and visualization.

We worked extensively with geo-scientists to understand the challenges of long running iterative modeling and simulation processes. In FY 2010, we developed the initial version of GS^3 as a software framework specifically for the carbon sequestration domain. We combined version control system with web-based Semantic Mediawiki to provide robust versioned data storage along with an interface to annotate, semantically tag, and search data. We developed metadata extractors to parse geologic well logs and present them visually using plotting tools and Google map interface.

GS^3 is a set of tools integrated through a software framework that supports the modeling process used to evaluate and monitor carbon dioxide sequestration sites. In FY 2011, we refactored GS^3 into Velo, a generic scientific knowledge management framework and deployed GS^3 as a carbon sequestration specific customization of Velo. This refactoring enabled the use of Velo across several scientific domains. Significantly, we realized that several scientific domains face challenges similar to the carbon sequestration domain. For example, many need the ability to parse large volume of initial data, document missing data and assumptions, keep track of data used, and be generated throughout the project life cycle.

Specific FY 2011 milestones include the following:

- Used a scalable content management system (CMS) to replace subversion based backend. In addition to version control, CMS provides advanced functionalities such as fine-grained access control, automated data extraction, and triggers.
- Used a module-based deployment process, enabling easy domain-specific Velo customization and extension.
- Created a tool integration framework that enables varied tools using simple xml-based specifications.
- Integrated tools created by other GS^3 focus area projects to support the modeling process.
- Provided initial provenance support such as saving named relationships between files/folder, static graph view of saved relationships, ability to group files into virtual collections, and automatic recording and inputs and outputs of tool invocation.

In FY 2012, we will focus on provenance, using interface to capture and visualize provenance data. For example, provenance record audit logs, rich interactive graphs view, and edit relationships notification based on file associations or tags. Additionally, tool integration work will improve the initial implementation of framework to support varied types of tools and make them provenance aware.

Integrating Power and Performance Modeling for Exascale Systems

Kevin J. Barker, Darren J. Kerbyson, Adolfy Hoisie, Abhinav Vishnu

◆ As large-scale parallel systems continue to increase in size and complexity, power will become a primary constraint in the design of both machines and software. We are exploring methods to quantify predictively the power consumed during software execution on a given platform through analytic modeling approaches as well as examine techniques to optimize power and energy consumption by attacking all levels of the software and hardware stack. ◆

Supercomputer systems have been designed primarily with performance as the main criterion that must be met. However, as we move towards the Exascale era, power consumption will increasingly provide the pressure that will drive system design. Simply scaling up current technology will not provide an acceptable solution; current estimates for power consumption of such as system range from the high tens to hundreds of megawatts, placing them outside the possibility of implementation. New solutions are required at all levels of the system architecture from hardware through middleware tools and to algorithms and applications with an eye towards optimizing both power consumption and achievable workload performance.

In this project, we approach the challenge from two vantage points. First, we are developing tools and techniques that will allow for the quantification and prediction of both the performance and power consumption of a given workload executing on a given hardware and software platform. To this end, we are developing methods that decompose an application's dynamic behavior into a set of atomic activities whose performance and energy consumption characteristics are well understood. Through a set of micro-benchmark kernels we are developing, we will determine the power consumption characteristics of the system and, in turn, map these characteristics to full-scale application behaviors. The goal is to define a power consumption model that captures the workload's full-scale behaviors and can be applied to current and future systems.

Second, we are developing methods for optimizing application power consumption using tools that are available today. Optimizing power and energy consumption is not simply a concern of the hardware; methods must be developed for maximizing efficiency at all levels in the system from the hardware through the system software and application. We are pursuing three tasks in this regard. At the hardware level, we are investigating the energy efficiency of GPU devices. At the runtime software level, we have explored methods for optimizing the energy efficiency of single-sided data transfer communication operations implemented in the ARMCI communication library. Finally, at the application level, we have developed *Energy Templates*, which encapsulate knowledge of per-core application runtime behavior in an analytic model in order to identify periods during execution during which energy may be conserved.

In FY 2010, we procured a measurement harness consisting of a power analyzer to gather measurements of power consumed by relevant workloads running on current and near-term future hardware. We performed and initial examination of the energy consumption of single-sided communication primitives, where we used an interrupt signaling mechanism and dynamic frequency scaling to down-clock processors. We found that in both cases, as message sizes increase, these methods produce improvements, showing reductions in energy consumption. Additionally, we leveraged existing relationships with major hardware designers (e.g., AMD and Intel) to gain access to the next-generation hardware and gathering data to characterize applications with different requirements (e.g., compute, memory, and network).

GPU hardware provides a clear performance advantage over today's multi-core CPU processors on a variety of compute-intensive kernels. Often, this compute performance comes at the cost of increased power consumption. What is less understood, however, is how GPU hardware fares in comparison with multi-core CPUs in terms of energy efficiency. With these challenges in mind during FY 2011, we utilized a system containing two Intel 6-core Xeon X5650 Westmere processors (with a clock speed of 2.67GHz) and four Nvidia Fermi C2050 GPUs. Results using a matrix-matrix multiplication kernel indicate that performance using a single GPU is substantially higher than when using all 12 CPU cores (~275GF/s vs. ~120GF/s on large matrices). Nearly equal power consumption also results in improved energy efficiency for the GPU (0.5GF/W vs. 0.27GF/W). However, increasing the GPU count from 1 to 4 does not result in improved energy efficiency beyond 0.7GF/W.

At the runtime software level, we optimized the energy efficiency of single-sided data transfer communication operations within the ARMCI library, which forms the basis of the Global Arrays toolkit. Given current technology, two methods are available to influence the energy consumed during data transfer: Dynamic Frequency Scaling (DFS) – altering the processor core's clock speed during runtime to conserve energy or maximize performance – and the data arrival signaling mechanism – using either a *polling* or *interrupt* mechanism to signal data arrival. Both are used to reduce energy consumption during the period in which the processor is waiting for the completion of an inter-processor

data transfer operation by either down-clocking the processor cores or through eliminating periodic and energy wasting polling operations to check for data arrival.

We conducted experiments using the ARMCI *Put* and *Get* operations in order to determine whether energy savings are possible using DFS and have identified saving of nearly 10% at message sizes of 256 KB. As the overheads associated with changing the processor's power states and servicing system generated interrupts decrease, and as a wider variety of power states are made available with more significant reductions in associated power consumption, we expect to see more substantial energy returns.

Finally, at the application level, we developed the concept of *Energy Templates* that encapsulate knowledge of per-core application runtime behavior in an analytic model in order to identify periods during execution where energy may be conserved. Given mechanisms such as DFS that reduce processor power consumption during periods of idleness, a key question becomes how and where to take advantage of these power saving features. For instance, a large class of applications exhibits a common iterative processing flow with iterations separated by global synchronization operations. When all processors are load balanced, this results in an execution pattern in which all processors arrive at global synchronization points simultaneously, resulting in very little incurred idle time. However, idle periods may result either for algorithmic reasons (e.g., data dependencies across processors) or due to an imbalance in the work across processor cores (e.g., as may result from adaptive mesh refinement).

Knowledge of application behavior can be exploited to identify *a priori* periods in which idleness is expected, and can then be used to guide the runtime system in making energy-conserving decisions. Such knowledge is held only by the application; without guidance, lower levels of runtime software are only able to react to periods of idleness once it can be identified, increasing the overhead associated with transitioning to low power states. *Energy Templates* allow processors to transition to lower power states immediately once new application phases are entered. Key principles of *Energy Templates* include:

- representing an application-specific sequence of active and idle states for each processor core which may vary from core to core
- containing the rules associated with the transition from one state to another using a model that represents the application's expected parallel activity
- making use of triggers that enable state transitions by transparently monitoring application activity
- enabling the runtime system to make informed decisions about whether or not to alter an individual processor core's power state.

The power-instrumented NW-ICE machine was used to measure the performance and energy savings of a wave-front application in which algorithmic design causes processors to remain idle while waiting for data dependencies to be resolved. Two power states are available corresponding to a core being either active or idle with a resulting 11 W power difference per core. With the greater differences in power states available on more current and future cores, the observed power savings is expected to be even greater than what we have observed here.

The execution time measured with and without *Energy Template*s is within 4%; this small difference is due to the extra overhead induced by the *Energy Template* and corresponding runtime software. The magnitude of power saving of 8% is significant but should be contrasted with the peak possible power savings predicted analytically of 23% on the test system. Increased power and energy savings occur using the *Energy Template* approach for this application as system scale and the differences in power states increase.

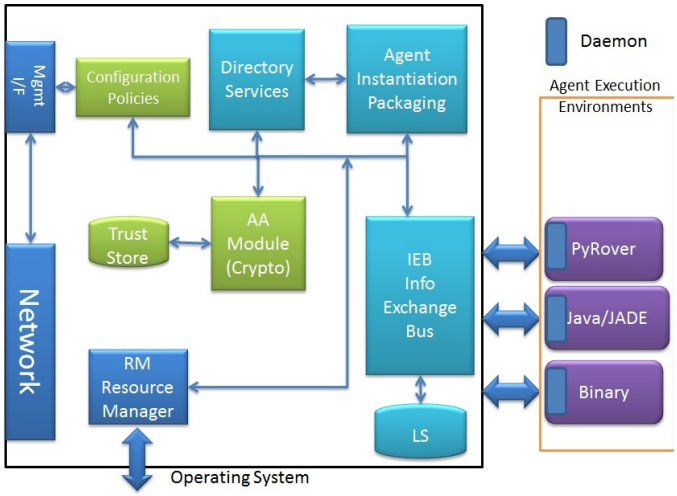
With our significant progress in the areas of modeling and optimizing power consumption at significant processor scales this year, we will continue this work in FY 2012. Additionally, the arrival of the institutional computing cluster will help dramatically in this regard during the upcoming fiscal year, as it will give us access to a large-scale system with measurement capability

Intelligent Networked Sensors Capable of Autonomous, Adaptive Operations in the Electric Power System

Bora A. Akyol, Philip A. Craig, Jereme N. Haack

◆ Our research project creates a framework to add "intelligence" to command-control driven sensors and actuators used in the electric power system today and forms the basis of a new distributed operations and control paradigm. ◆

The number of intelligent devices (including sensors) connected to the electric power system is expected to increase several orders of magnitude by 2020, but our ability to utilize them is not keeping pace. Our research project creates a framework to add intelligence to the sensors, which manifests itself in the capability of adjusting measurement methods and in the functionality of performing measurements in multiple dimensions such as information networks and electric power system simultaneously. The ability to observe and correlate measurements from multiple domains will significantly improve the cyber security of control systems used in the electric power system. These intelligent sensors are capable of sharing information through the various layers of the electric power system to enable two-way power flow to facilitate integration of distributed generation as the power systems of today are unable to accommodate distributed generation capabilities due to lack of system flexibility and concerns about system stability. Finally, when paired with distributed autonomous controllers, sensors can form the basis of an intelligent system that supports micro-grids and islanding.



The Intelligent Device Platform provides a secure, robust, resilient framework that allows software agents to be deployed for control and monitoring in the electric power system.

Our research will lay the information network groundwork for distributed operation and control of the electric power system especially at the distribution layer where end customers are being served. The intelligent sensors and the distributed control paradigms enabled by this intelligent sensor cloud improve system reliability and support integration of distributed generation.

Our most significant deliverable for FY 2011 was a design specification for the intelligent sensor software framework. The design specification is important because it allows us to start implementing the intelligent sensor platform in FY 2012. We have used software prototyping as much as possible to reduce execution risk and to verify that our design is correct. Based on our research, our prototyping efforts, use case, and requirements analysis, we converged on the design of a software platform that can be used to enable distributed intelligent devices in the electric power system. The key strengths and distinguishing factors of our software platform are that it is hardware architecture agnostic (requiring a modern CPU with MMU support) and supports multiple software agent execution environments simultaneously. We also have the ability to monitor resource utilization and terminate misbehaving agents. Our software platform provides robust security even when network connectivity is disrupted and provides distributed, decentralized directory services for location functions and agents. As part of prototyping efforts, we developed a simulation in Netlogo to validate our methods and the behavior of our software agents.

During the last fiscal year, we published a paper for the ASME ESFUELCELL that was well-received. One of the needs for our software validation efforts was a highly scalable network simulator. For this purpose, we performed a comprehensive network simulator survey, which will be presented during HIPCNA-PG 2011 at the SuperComputing 2011 conference. The survey performed has allowed us to choose a simulation and execution platform for FY 2012.

In FY 2012, we will start implementation of base sensor platform and integrate with other codes. A hardware demonstration our intelligent sensor platform will be created. This demonstration will showcase collaborative agent behavior and will also leverage FPGI GridOPTICS powerNET laboratory as equipment becomes available to demonstrate and show the operations of the sensor software platform. One of the challenges in deploying large numbers of autonomous devices is their management. To address this problem, we will produce a design specification for scalable,

policy-based, context-aware management platform for intelligent sensors, including management schema, communication protocols and sensor lifecycle management. We will also identify operational conditions that require autonomous system to human-in-the-loop transitions. As a use case, we will design and prototype a hybrid decentralized sensing, reasoning, and actuation system that incorporates Bayesian inference networks and mobile agents to address identified use cases. This agent system would serve as an example application for the software platform being developed on this project.

Linear Algebra Solvers and Associated Matrix-Vector Kernels for Power Grid Simulations

Barry Lee, Stephen T. Elbert, Mahantesh M. Halappanavar, Uditha C. Bandara

◆ This project researches the development of advanced linear solvers and matrix/vector kernels that are a key enabler for power grid modeling through high-performance computing simulations. These advanced solvers and kernels will enhance modeling capability for current and future power networks utilizing high-performance computing. ◆

DOE's Office of Electricity has invested heavily in the investigation of more flexible, reliable, and higher capacity electric energy infrastructures that incorporate new engineering technologies (e.g., sensors and renewable energy sources), and other DOE program offices have invested in high-performance computing facilities to advance science applications through computer simulations. The purpose of these investments is that modeling and computer simulation will play a major role in the fundamental and applied research in advancing the future power grid systems. As these systems and their models increase in complexity and size, the utilization of high performance computers will be a necessity. In particular, high-performance computing will be needed to solve efficiently the mathematical equations underlying the more complex power grid models of the future. In the past, for less accurate models, simpler equations were often solved using commercial software packages and on desktop computers. For advance models, to obtain the solutions to these mathematical equations, carefully designed parallel solution procedures that utilize high-performance computing will benefit the simulation capabilities.

The computational bottleneck of these solution procedures often arise in inefficient linear solvers and matrix-vector kernels. Thus, the purpose of this project is to develop efficient, stable linear solvers and computational kernels for power grid applications simulated on high-performance computing. This efficiency is measured by both fast turnaround time for the linear solvers and matrix-vector kernels to perform their operational tasks and their ability to utilize the computational resources on the high-performance computing (e.g., large problems solved by careful usage of more computational resources give faster turnaround time than when solved using less computational resources). This stability is a measure of the solver's ability to generate accurate solutions to the equations. Unfortunately, due to the mathematical properties of some equations, the numerical process of many solvers can dramatically amplify small errors to make the solutions totally invalid. One such relevant power grid application that leads to these undesirable properties in the mathematical equations is state estimation. Thus, the target goal of this project is to develop quality efficient and stable linear algebra software for power grid applications.

Successful completion of milestones included the following: several computer simulators were developed and implemented to generate some of the linear systems and matrix-vector operations arising in power grid applications. These simulators are a necessary step because they both generate the linear systems that arise in the power grid applications and expose the appropriate data structures that can better utilize high-performance computing. Generation of the linear systems also allow us to determine the design of the appropriate linear solvers and matrix/vector kernels; determination of the appropriate data structures allow us both to achieve better parallel efficiency and to develop a natural user-friendly interface into the linear algebra software.

With these simulators developed, our next step was to develop and simulate several linear solvers and matrix-vector kernels. A simulator for dynamic state-estimation via Kalman filtering was implemented, and for these linear systems, several iterative solvers that solve blocks of linear systems were developed; specifically, a simulator for static power flow state-estimation that performs the whole process on parallel was implemented and, for the systems arising from this application, a stable iterative solver (a bi-diagonalization method). The solver for this latter application solves rectangular least-squares problems directly, which permits better stability. During FY 2012, further research and development on even more efficient high-performance computing utilization will be conducted (i.e., better parallel matrix-vector kernels, better solver processor scalability, and preconditioners for least-squares systems).

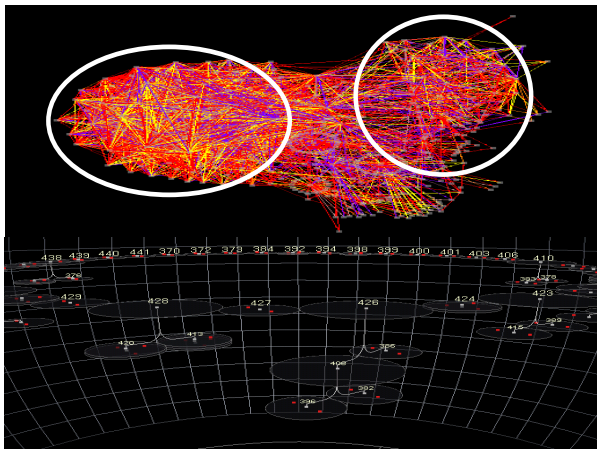
Research has also been started on a different linear algebra issue, the eigenvalue/vector problem, arising from the small-signal stability application in power grid modeling. Investigation into the current state-of-the-art eigenvalue/vector techniques used in the power grid community, and the current state-of-the-art in the mathematics/computational science community has been conducted. In FY 2012, development and implementation of these eigenvalue/vector solvers will be performed.

Machine Learning String Tools for Operational and Network Security

Christopher S. Oehmen

◆ The goal of this project is to move toward proactive exploit detection by applying the mathematics and theory of bioinformatics. This approach is based on 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, analyze software binaries and files, 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, a challenge in the face of constantly evolving exploit methodologies.



Top: Network view of similar servers illustrates commonly behaving servers on the PNNL network; bottom: Hierarchical cluster of servers indicates high-confidence server families.

This project is directed at developing capabilities to enable the construction of a collection of solutions to challenges in cyber and network security. The goal 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, evolving relationships between text strings associated with digital information and use machine-learning principles to extract patterns without *a priori* knowledge of those patterns. Success would have significant operational impact by enabling pattern-based, data-driven identification schemes grounded in a theoretical framework to augment the current rule-based approaches to cyber security. The intent is to develop the algorithmic and computational infrastructure needed to deploy this concept rapidly into new problem spaces of cyber security.

Starting with FY 2008, we developed and implemented vectorization strategies for network transactions. FY 2009 brought a feasibility study for classifying cyber events, improving the vectorization strategy from the previous year and creating a strategy for HPC binaries. We also worked on algorithm development to optimize the training phase. In FY 2010, we completed the ingestion/translation pipeline and demonstrated analytical capabilities on cyber data.

In FY 2011, we focused on exploring an alternate method for file analysis based on differences in binaries measured with Xdelta3. We hypothesized that the number and size of copy commands in Xdelta3 output could be used to create a metric of similarity between two binary files. We further explored the distribution of copy commands in Xdelta3 output from binaries of varying levels of similarity. To create a similarity metric from the copy command statistics, the number and size of copies for a comparison of two unrelated files would require the same distribution, modulo some normalization for file sizes. If this were true, then comparing the distribution of copy commands for any two files to the expected distribution for unrelated files should yield a metric of the degree to which the distribution in question did not fit the distribution of non-relatedness. We performed two tests to evaluate the hypothesis.

For the first test, we used a collection of 456 binary files with an unknown distribution of similarities. For the second, we created a test set that consisted of 50 binary files with randomly generated sizes between 40 KB and 30 MB. For both tests, we used Xdelta3 to generate measures of how many copy and move commands are required to transform one file into the other. Our hypothesis was that the attributes of these transformations could be used as a similarity metric for arbitrary binary files. However, we found that copy is rarely used when files are different beyond a moderate amount, and the add command is used instead. This means that copy is not a reliable distance metric for arbitrary binaries unless they are similar to begin.

It seems clear from these tests, the pattern of copy commands we expected to see between more distantly related binary files will not materialize. Upon further analysis, we suspect this is because unlike a proteomics approach to sequence comparison, which looks for small substitutions within a larger pattern, Xdelta3 looks only for exact matches of byte sequences.

Mapping Molecular Dynamics Algorithmic Parallelism to Heterogeneous Architectures

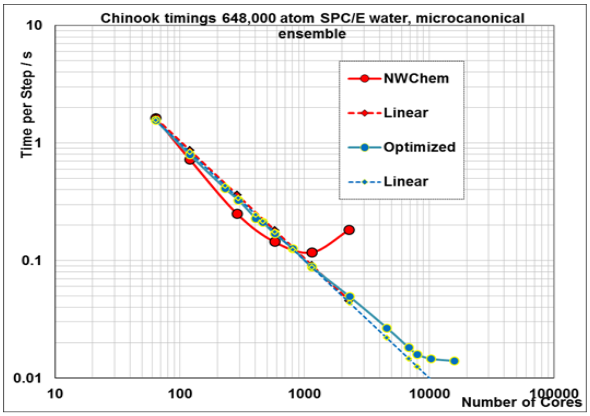
T.P. Straatsma

◆ Novel computer science and software engineering approaches are applied to develop a high-performance molecular dynamics (MD) modeling and simulation implementation for biomolecular modeling research. ◆

A principal and general challenge for biomolecular modeling and simulation in support of environmental molecular science involves the generation of extended molecular trajectories. The trajectories use advanced simulation methodologies to capture those features central to the research questions being addressed. This applies to understanding important biological processes relevant to human health and environmental issues such as carbon cycling and energy security by creating fuel from biomass. The molecular-level processes to be understood through application of computer simulation include protein folding, protein docking, complex enzymatic reactions, and the association and function of large protein and protein-DNA complexes. The common situation in all these cases is the need for sufficiently large ensembles of conformations to capture the relevant events, which requires highly efficient computer codes to be designed and applied on the largest supercomputers. Achieving high scalability to remove current bottlenecks in applying MD simulation codes on very large processor count computer architectures is approached by formulating an implementation strategy that leads to significant performance improvements and through an extensive analysis of the algorithms used.

We propose to design new computer science and software engineering approaches to develop a high performance molecular dynamics modeling and simulation implementation for biomolecular modeling research that is aware and takes advantage of the specific characteristics of the underlying architecture to achieve scalable performance on the very large processor counts that can be expected to exist in the next generation extreme scale supercomputers. We will also use performance modeling and analysis to design new implementation strategies for latency hiding, communication improvements, data structure optimizations, and single node performance optimization.

Based on a domain decomposition approach, we have designed a new data structure to exploit locality and reduce communication and memory requirements. This approach allows a number of processes to be used of at least 14 times the number of cells in the system. The most important challenge for scalability of classical MD is the need for synchronization after the evaluation of forces and after updating the coordinates. Large process counts make the use of global synchronizations, which is acceptable on simulations using less than 1,000 processes, very inefficient. In the redesigned kernel, synchronization is made implicit by processes waiting for the number of expected neighbor contributions before continuing. This implicit local synchronization approach effectively "buffers" operating system jitter, resulting in much improved scalability.



Wall clock timings for a 648,000-atom SPC/E water simulation using the cell-distributed NWChem MD module and the newly designed cell-cell pair distributed kernel.

With the approach described above, a new MD kernel was designed and used to investigate effective communication approaches for a homogeneous system simulation. Timings are provided for a 648,000-atom MD simulation of SPC/E water in the micro-canonical ensemble, as obtained on EMSL's "Chinook" HP/InfiniBand cluster. Scalability for this system using NWChem, which is based on the distribution of cells, levels off at 1144 cores. The newly designed kernel scales for the same system to 16,000 cores. In both simulations, one core per node was reserved for the Global Arrays/Aggregate Remote Memory Copy Interface server thread, which is necessary to effectively deal with the communication requirements of these simulations. Compared to the NWChem runs, the new kernel scales to an order of magnitude more cores and results in a wall clock time per step an order of magnitude smaller.

Research plans for FY 2012 include the development of SMP-node optimized parallel implementations using threading and/or GPUs of the loop structures of the force evaluation and the implementation of long-range electrostatic force corrections using an algorithm that avoids synchronous operations in the setup of the charge grid.

Multi-Resolution Data Model and Directed Data Reduction, Reconstruction and Aggregation

Kerstin Kleese van Dam, Terence J. Critchlow, Tara D. Gibson, Ryan P. Hafen, Mark J. Rice, A.V. Kulkarni

◆ This project will develop a prototype multi-resolution data model and example directed real time data reduction, reconstruction, and aggregation capabilities that will enable real-time situational awareness of the future power grid throughout its various levels. ◆

The future power grid will require bidirectional, real-time data flow to identify and respond to changes in demand, including quick reaction to extreme events, operational monitoring, daily and medium-term operational planning, and long-term facility planning. Unlike the current grid with a relatively small number of power sources, the future grid will have thousands of potential sources, including hybrids, wind sources, and solar panels in addition to traditional sub stations and power plants. Each of these sources will operate independently and thus respond differently to fluctuations in price, resources, and operational circumstances. Consumption devices will also be smarter, using real-time pricing to make decisions about their level and timing of consumption (e.g., an air conditioner will cycle on depending not only on current temperature compared to the desired, but also the current price of electricity). Each of these production and consumption units as well as the connecting power infrastructure will be equipped with smart sensors that not only report on status and deliver operational information, but are also receptors of information and instructions (i.e., reduce demand/production).

In this project, we are researching methods and protocols for sharing information between co-located sensors to improve the quality and reliability of the measurements being performed. We anticipate delivering a multi-resolution data model for the power grid and associated, situation-directed data reduction, reconstruction, and aggregation methods with integrated information on data quality and uncertainty. Specifically, we will develop a semantic data infrastructure capable of identifying events of interest from within power system data, including PMU data, and efficiently retrieving those events and the associated raw data through an API. This comprehensive infrastructure will enable analysis programs to access events of interest effectively from large historical data repositories and, as a result, will increase their effectiveness.

Our initial focus of this project in FY 2011 was on the specification of requirements for a multi resolution data model for data transport in the power grid that compressed, identified features and prioritized data for transfer based on the importance of the data and the requirements of the receiver. In particular, our initial research investigated appropriate data compression techniques and quantified the data transfer requirements. Based on this evaluation, we focused our ongoing research on ensuring historical information will be readily accessible to the engineers, and their analysis tools, for comparative analysis, enabling them to quickly answer important questions. This requires a data infrastructure that can be quickly searched to retrieve relevant historical information on very short time scales.

Our approach to data compression was to develop a predictive algorithm that anticipated the next measurement on a data stream, took the difference between the predicted and actual values, and compressed the difference instead of the actual value. If the predictions were perfect, only a single bit (0) would represent the difference and the data stream would not need to be transmitted at all. Of course, the predictions are not perfect so some data transmission will always be required. However, our preliminary results were extremely positive. Using short but real PMU data streams, we obtained between 40% and 50% lossless data compression, a significant improvement compared with compression rates of traditional compression algorithms, which were approximately 20%.

To understand the transmission requirements, we established an estimate of the eventual bandwidth requirements for the transmission system. Each PMU sample is 48 bytes, with 60 samples per second. Our best estimate is that there will be a maximum of 50k PMUs distributed across the nation when fully deployed, which leads to an aggregate national bandwidth requirement of 144MB/sec. Given current communications protocols (e.g., 10GigE, 802.11n), our analysis implies there will be no bandwidth issues in transporting the data generated by the PMUs. We have published a paper documenting this conclusion (CIGRE2011). We also found that the ability to retrieve relevant historical data quickly does appear to be a significant problem at the expected data volumes. In particular, the problem arises from the difference between the semantics of the raw data and the semantic abstractions that power engineers and analysis tools would prefer to query. Addressing this problem will be the focus of the remainder of this project.

To start, we identified ten queries of interest that will ground the development of our data infrastructure. These queries are representative of classes of queries of interest to power engineers and based on our projected ability to identify islanding events within available PMU data. Specific queries that we are targeting for our infrastructure are as follows:

- Is the island stable?
- How big is the island (number of PMUs)?
- What is the frequency difference between the partitioned areas?
- Which PMUs have been involved in the most islanding events over the past N months?
- Which events occurred within N hours?
- Find the islanding event in the past year which lasted the longest.
- Are there PMUs which tend to form an island?
- What generators exist within an island?
- Show me the raw data from PMUs within an island.
- Find all islanding events in which a specific PMU was inside of the island.

During FY 2012, we will focus on design of a metadata generation capability and the definition of our semantic data infrastructure and API. Metadata generation is the process of converting an in-depth analysis of the data into higher level information that can be used to answer specific questions. This will be accomplished by performing exploratory analysis of historical PMU data to identify events of interest and developing rules that allow instances of these events to be automatically extracted.

Our target architecture will be selected in early FY 2012, after which we will concentrate on implementing a prototype that will be able to effectively store the metadata, perform complex searches, and return results in a format capable of supporting iteration with the metadata generation step. Once the initial prototype has been developed, we will focus on refining the API and optimizing the query response time for the most common queries.

Multiscale Models for Microbial Communities

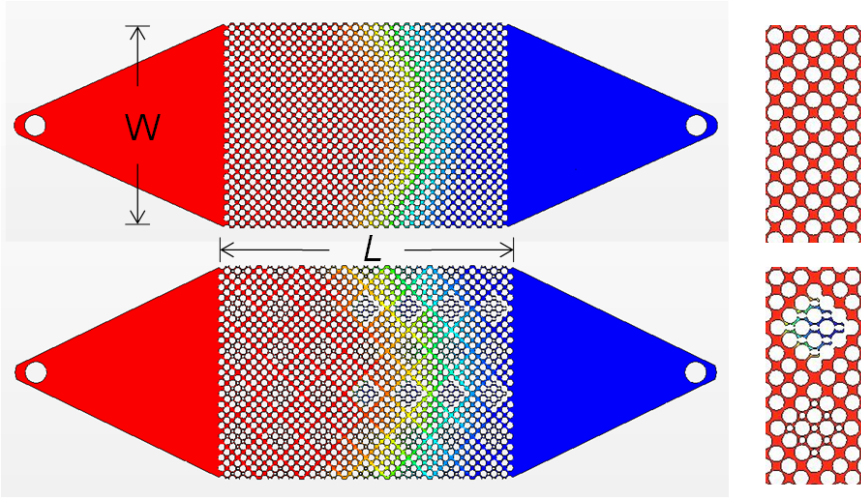
Haluk Resat, Allan E. Konopka, Vanessa L. Bailey, Lee Ann McCue, Marshall C. Richmond

◆ This project will develop mathematical models that incorporate the possible effects of heterogeneous three-dimensional structure, functional biodiversity of the microbial population, and geochemical processes into a unified model to improve our understanding of the role of interactions between co-existing organisms in a microbial community. ◆

Soil is a highly complex heterogeneous system in terms of inhabitant microorganisms and spatial properties. Soil structure can be viewed as a dynamic hierarchy of sizes that contain microbial cells with different metabolic properties. Such variations in local environmental conditions are expected to lead to a widely varying distribution in microbial cell dynamics. For mathematical modeling, this translates to having a heterogeneous system in which participating objects have different classes of dynamic properties: some would show strong individual characteristics that require explicit treatment, some would be part of multi-cellular assemblies that mimic large well mixed systems, and some would be endure in-between conditions.

Metabolic activity of microbial organisms depends on the local environment conditions. At the microscale, microbes may encounter highly heterogeneous living conditions because of the environmental restrictions. The aim of this project is to develop mathematical models that incorporate the possible effects of the heterogeneous three-dimensional structure, functional biodiversity of the microbial population, and biochemical processes into a unified model to improve our understanding of the role of interactions between co-existing organisms in a microbial community. This project contributes to predicting the impact of microbial community based management practices in controlling and regulating carbon flow in soils. How variations in the local environmental conditions and the cellular interactions with their surroundings affect the dynamics of microbes is investigated using two example systems in this project: microfluidic devices for micromodel communities and porous soil-aggregates for natural settings.

Using the metabolic network model that we developed during prior years, simulations were performed to predict which type of cellulose degradation mechanisms might give survival and growth advantage to bacterial organisms in the soil system. Different strategies for acquisition of soluble carbon substrates from polymeric cellulose were investigated. We found that bacteria that express membrane-associated hydrolase had different growth and survival dynamics in soil pores than bacteria that release extracellular hydrolases. Observed differences suggested different functional niches for these microbial types in cellulose utilization. Our model predicted an emergent behavior in which co-existence of membrane-associated hydrolase and extracellular hydrolase releasing organisms led to higher cellulose utilization efficiency and reduced stochasticity. Their co-existence was mutually beneficial to the organisms where the initial cellulose degradation activity by membrane-associated hydrolase expressing cells shortened the soluble hydrolase build up time and, when enzyme build up allowed for cellulose degradation to be fast enough to sustain exponential growth, all the organisms in the community shared the soluble carbon product and grew together.



Microfluidic simulations showing how fluid flow carries the soluble substrates through the device. Substrate is injected from the inlet on the left. Figure shows the transport rate of the substrate at the central plane of 75 micron thick device when the moving front is halfway through the device. Dimensions were L=22 mm, W=16 mm, and the distance between inlet and outlet connection sites (circular areas at the tips) was 52 mm. The left and right ends correspond to the maximum and zero transport rates, respectively. The top located design i includes uniformly aligned, circular vertical columns; the bottom includes islands with narrower passage ways and blocked pores. Sections of the pictures are shown enlarged on the right.

Microfluidic devices offer unique advantages in biological research that their interior geometry can be designed to have growth regions and

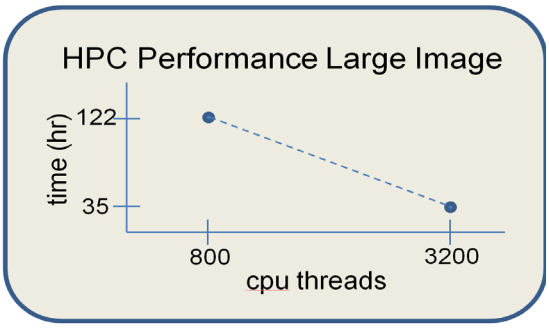
flow channels with sizes as small as a few microbial cells where the fluid flow rate can be adjusted to vary the local substrate availability. Local concentrations of the soluble substrates would depend on their net consumption rate r (cellular consumption minus substrate production) in the reactions that they participate in and on their net input rate f by the fluid flow. Balance between these processes determines if local concentration can increase ($f>r$), diminish ($r>f$) or a quasi-steady state can be formed ($r\approx f$). Because the validity of each condition would depend on the local flow profile and on the cell biomass levels, with the appropriate device design, hydrodynamic flow patterns can be taken advantage of to create substrate rich and poor regions within the microfluidic device. We are particularly interested if oxygen gradients can form within the devices because they may result in oxygen-poor anaerobic regions that co-exist with the oxygen-rich aerobic regions. We have pursued computational fluid dynamics simulations to determine the flow patterns for different structures. These simulations have confirmed that, for certain designs, one can obtain low advective flow zones within the device (see figure), which implies that anaerobic regions can indeed form if the inoculated biomass is high in those areas even when the fluid is flowing through the device.

We will continue to use model predictions to aid the design of experimental studies that are pursued in complementary projects. Our future studies will investigate the dynamics of model microbial communities in microfluidic devices and in natural systems to determine which physical and chemical environment characteristics impact the microbial community dynamics.

Nanoscale-Macroscale Three-Dimensional Integration Using High Performance Computing

James P. Carson, Andrew P. Kuprat, Simon H. Kahan, John T. Feo, Daniel R. Einstein

◆ This work seeks to establish the capability to generate three-dimensional (3D) datasets of macroscale data at nanoscale resolution by collecting multiple serial two-dimensional (2D) images at nanoscale resolution and developing the high performance computing software to reconstruct the data. The capability to associate nanoscale events rapidly into the context of the macroscale is essential to achieving greater innovation multiple disciplines. ◆



Processor count scalability on the Cray XMT using parallelized image registration code.

Systems biology assumes that a life form by interactions between genes, macromolecules, and cells, which do not act alone. In fact, systems biology presupposes that the spatial organization of specialized cells working closely with their neighbors determines the functional and structural attributes of an organ. Technological advances in the tools used in systems biology have led to an explosion of information that has changed our approach to the study of disease. This includes the complete sequencing of genomes for many different organisms; the development of sophisticated tools for generating genomic, proteomic, and metabolomic data; and the development of interactome network maps. A significant limitation of these techniques is that they present a static snapshot of cellular events with no spatial information. The capability to rapidly associate nanoscale events into the context of the macroscale is essential to achieving greater innovation in research.

This research will bring genes, macromolecules, and cells imaged at sub-micron spatial resolution into the context of a 3D organ system. Using high resolution histological techniques, a small organ, organism, or bacterial population can be fixed, serial sectioned, treated with specific cellular and/or sub-cellular identifiers, and digitally imaged at 230 nanometers. These images can be computationally stacked into a volume representation at subcellular resolution.

Development of this capability is part of the emerging field of bioimage informatics. Although 2D image registration for small images is a generally available capability, generating 3D datasets from images at this resolution and scale is not known to exist at any institution worldwide. The primary impediment to recreating a volumetric image of histological data at subcellular resolution is that the images are extremely large. Each image can be up to 100 GB in size, and an entire volumetric dataset can occupy over a petabyte of data. Fortunately, 3D reconstruction of deformed tissue sections is a highly parallelizable task that can make efficient use of high performance computing resources.

In collaboration with Dr. Charles Frevert at the University of Washington, we have started production of serial sectioned multicellular pulmonary datasets. Each image in these test datasets is ~ 80000 × 80000 pixels in size, which is the equivalent to the image size produced by a 6400 megapixel camera. These datasets represent different embedding conditions, various sectioning distances, and two different organisms: mouse and rat. By acquiring datasets under these different variables, the effects of these variables on computational performance can be examined. Then, the optimal experimental conditions can be determined for future data collection efforts.

An image registration algorithm based on optical flow calculations was compiled and tested on the Cray XMT supercomputer for a pair of small test images to ensure proper functionality of the registration. During this, the source image successfully deformed to match the target image. Next, the registration function code was re-written to be suitable for parallelization and Cray-specific parallel command-calls were added. Good scalability on a large number of threads was observed; increasing the number of central processor unit threads to 3200 from 800 (4:1) decreased calculation time by 71% (3.5:1) for registration of large images. Additional optimization efforts continued to improve performance.

Warp-smoothing is an essential step during 3D reconstruction to retain the proper overall shape of the 3D sample. To begin implementation of this step, an initial 3D reconstruction of a low-resolution version of a test dataset was created by applying an initial iteration of the warp smoothing approach. In addition, we tested the application of

calculated elastic registration warp grids to annotated locations within the test dataset. This will allow features detected in the unaltered data to be properly translocated into the reconstructed dataset.

For FY 2012, this project will implement a new capability, specifically, a massively parallel software tool for applying 2D rigid and elastic registrations pre-calculated by an optimizer to full scale images. An algorithm will be derived for calculating the optimal use of image scale and registration parameters for these pre-calculations, based on image data characteristics and processor threads available. In addition, optimization of parallel implementation of optical flow registration method will continue. Efficient and accurate warp smoothing algorithms that minimizes reliance on iterative calculation of warps from images will be designed and implemented. Collectively, these future project milestones will establish the capability for 3D reconstruction of macroscale specimens at nanoscale resolution using high performance computing resources.

Real-time High-Performance Computing Infrastructure for Next-Generation Power Grid Analysis

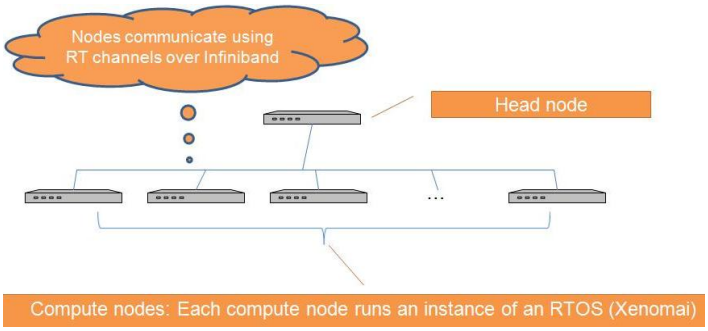
Peter S.Y. Hui, Yousu Chen, Satish Chikkagoudar, Mark R. Johnston

◆ We are developing a platform for real-time computation in a high-performance computing environment with the context of supporting real-time future power grid analysis. Specifically, we aim to provide a real-time operating system for high performance computing machines along with real-time libraries to support key power grid analysis kernels. ◆

Real-time computing has been traditionally considered in the context of single-processor and embedded systems. Indeed, the terms real-time computing, embedded systems, and control systems are mentioned in closely related contexts. However, real-time computing in the context of multi-node systems (specifically high-performance, cluster-computing systems) remains relatively unexplored, largely because until recently, a need has not existed for such an environment. With the future power grid growing significantly, high-performance computing (HPC) platforms are integral to analyzing the grid. This project investigates infrastructure necessary to support cluster computation over large datasets in real-time. Our motivating example is an analytical framework to support the next generation North American power grid, which is growing both in size and complexity. With streaming sensor data in the future power grid potentially reaching rates on the order of terabytes per day, the task of analyzing this data subject to real-time guarantees becomes a daunting task that will require the power of high-performance cluster computing capable of functioning under real-time constraints.

FY 2011 was largely spent building up the infrastructure's foundation. We scoped the requirements for a small cluster computer on which to do our research and development. As a result, the cluster purchased was five-nodes: one head node plus four compute nodes, each with 2.66 GHz Quad-core Intel chips, 12 GB RAM, and 500 GB hard drive space. We also purchased one Infiniband switch and one Ethernet switch.

To achieve real-time constraints in a cluster computing environment, there are three general operating phases: first, data must be distributed to the compute nodes, subject to real-time constraints; second, the compute nodes must be able to compute their results locally, again subject to real-time constraints; finally, the local results must be aggregated to compute the final solution, again in real-time. In a traditional (non-real-time) cluster environment, the first and third of these would be accomplished using a data transport API such as MPI (Message Passing Interface). However, a real-time environment would require an analogue of an MPI subset, a component that does not currently exist and which we will ultimately develop as part of this project. Toward this goal, we spent part of FY 2011 developing a traffic prioritization API for the Infiniband hardware interconnect. This API will ultimately enable higher priority traffic to be transmitted with higher precedence than that of lower-priority real-time traffic.



High-level overview of targeted infrastructure. Compute nodes run a local copy of an existing real-time operating system (e.g., Xenomai), while data is moved between nodes via a real-time Infiniband layer, developed as part of this project.

The second of the aforementioned phases requires a real-time operating system (RTOS) to be deployed on each of the cluster's compute nodes. We evaluated several candidate operating systems, including RTLinux, Xenomai, and RTAI. The resulting evaluation led us to select Xenomai, as the RTOS of choice for a number of reasons, including its support for hard real-time deadlines; its simple, clean, effective ("user friendly") API; and its relatively wide and active user community. We installed Xenomai on two of our four compute nodes, giving us a configuration in which half of our compute nodes run a standard (non-real-time) OS, and the other half run a real-time OS.

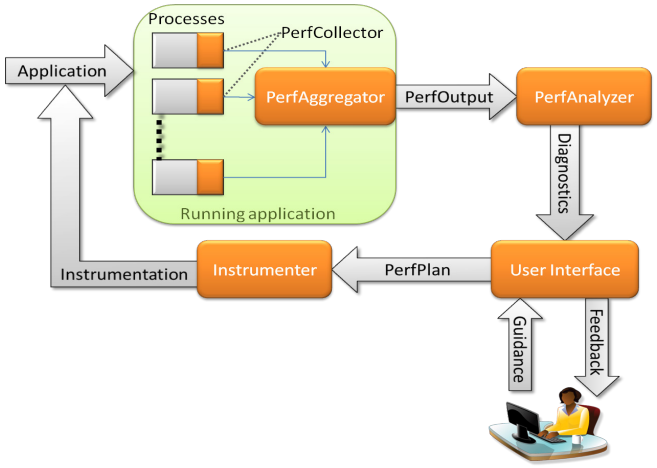
In any software framework providing correctness, a formal method of proving guarantees is typically provided in the form of a system model checker. While this area has been previously studied in depth, existing systems do not account for the intricacies that we face in a grid computing environment; therefore, model checkers will be at the forefront of FY 2012 activities. Additionally, to operate subject to real-time constraints, software must be integrated into Xenomai's real-time kernel, which will require some modification and rewriting pieces of the Infiniband software stack and the targeted power grid kernels to operate in this manner. To this end, we will integrate the software stack and sample power grid kernels into the RTOS real-time kernel.

Scalable Performance Diagnostics and Feedback for Massively Parallel Computers

Sriram Krishnamoorthy

◆ The effective utilization of current and future supercomputers for science requires an application performance at scale. This project aims to develop capabilities to identify performance bottlenecks quickly and inhibitors of scalability, focusing on inter-process communication. ◆

While characterizing communication behavior has been widely studied, a fundamental limitation of existing tools and approaches has been the limited usability in parallel programs running on large numbers of processors and the inflexibility in the information collected. Among the issues encountered are overhead to the profiled running program, managing the sheer size of the profiles generated, and providing insightful feedback to users rather than flooding them with raw data. Improvements in single processor performance through an increase in clock speed have been severely limited by the problems of power consumption and dissipation. High-end computers used for large-scale scientific calculations employ increasingly larger processor counts to achieve greater performance. The future exascale computers can be expected to contain up to millions of processors, with their complex interaction further complicating application scalability.



The envisioned iterative optimization process. We developed and provided support for GAs at each stage to enable effective application performance tuning.

We are addressing these issues in the context of the global arrays (GA) programming suite, the model used to develop key applications at PNNL. This project targets development of suite capabilities to identify performance bottlenecks and inhibitors of scalability. We will increase understanding of the application characteristics through profiling to provide insights into their performance on future parallel systems. Additionally, we will develop capabilities to identify the inhibitors of scalability in parallel applications. Our approaches aim to allow better tuning of application performance, which will reduce time spent in tuning, allowing users to focus on newer functionality.

In FY 2009, we developed a scalable communication trace compression technique. This unique approach extended a popular text compression algorithm to locate and compress identical patterns of communication across processes participating in the parallel execution. The results obtained from the combined algorithm were submitted for publication. In FY 2010, we developed multiple tools and extensions described below to support capabilities required in the tuning process.

- *Instrumenter*. Generator was used to develop a variety of ARMCI/GA wrappers.
- *PerfCollector and PerfAggregator – communication trace; compression* and *profile collection*. Communication traces retain the temporal order of communication operations; developed a preliminary version of a profile collection framework.
- *Tool integration*. We developed support for ARMCI profiling in TAU and SCALASCA, two widely distributed tools *employed* to profile MPI programs.
- *Application evaluation*. The artifacts of this work were used to characterize a key module in NWChem using the TAU performance system.

In FY 2011, we built on the research conducted in 2010, extending support for ARMCI in SCALASCA to develop a performance pattern to evaluate the impact of waiting for progress in ARMCI programs. This work showed the need for passive progress in application programs based on the remote memory access programming model. The results were published in the inaugural International Workshop on High-Performance Infrastructure for Scalable Tools. We have also been invited to submit this work in a special issue of the *Journal of Parallel Computing*.

The support for ARMCI in TAU has been strengthened and is now available in the TAU public distribution. The wrappers developed for ARMCI and GA API are now available for use beyond the initial audience of the project, showing its wider utility. The profiling of NWChem identified the load imbalance cost due to frequent barriers in the NWChem CCSD calculation. This motivated the optimization of the iterative Coupled Cluster methods. The results were part of publications in both the Supercomputing 2011 Conference and the *Journal of Chemical Theory and Computation*.

Scalable Sensor Data Management Middleware

Jian Yin, Ian Gorton, Anand Kulkarni, Bora A. Akyol, Selim Ciraci

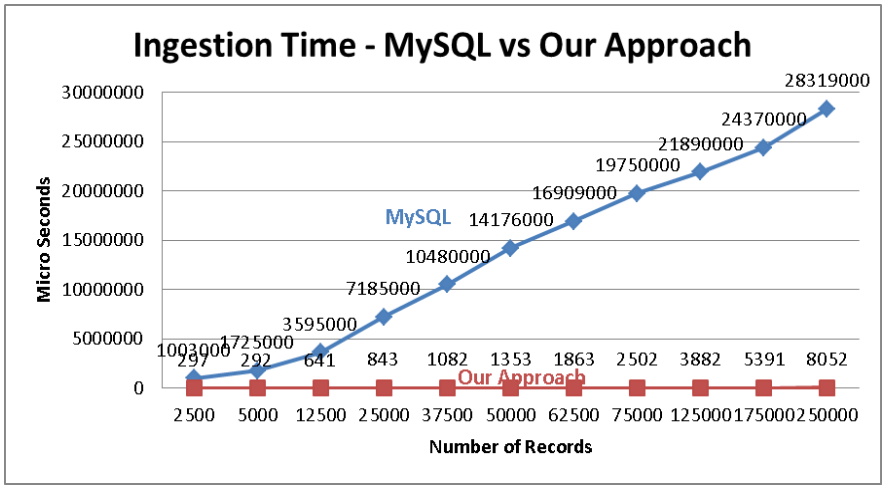
◆ This project is motivated by the explosive growth of sensors in power grid systems and an increasing number of innovative analysis applications that can utilize the sensor data to improve operation efficiency and increase reliability of power systems. These analysis applications not only need to access a large amount of sensor data from a large number of sensor sources but may also require the data to be delivered in real time. ◆

Smart grid technology promises to enhance and automate the monitoring and control of electrical distribution and is essential to integrating variable renewable energy sources that will reduce carbon emissions and enhance energy independence. To fulfill the lofty potential of smart grid, an unprecedented amount of data must be collected to understand the human and device behaviors that enable efficient distribution and consumption of electricity. However, these data are not useful unless they can be made available for analysis to understand control decisions and turn them into information and knowledge. An integrated data layer to mediate the massive amount of data and the large number of applications is the only viable option to provide efficient access to a large number of applications.

In this project, we built scalable, flexible data management middleware to collect, select, store, replicate, preprocess, and deliver the data generated from a large number of sensors deployed in smart grid systems. Our middleware is aimed to provide a general set of abstractions to meet the data access needs of a large and diverse set of analysis and control applications. We gathered design requirements of real-time data middleware for future power grid systems to handle the explosive growth of sensors and control and analysis applications that use these sensors to improve the efficiency and reliability of power grids.

Our system is designed for scalability and predictability to meet real-time requirements, and the storage is optimized for rapid insertion and deletion of high-speed data from a large number of sensors. Specifically, we designed a specialized log structure-inspired storage schema to store power grid sensor data. The data are written directly to the file system block device layer using block device interfaces, eliminating high overheads and unpredictability associated with higher level interfaces such as file systems, in which one access can lead to multiple disk accesses for reading the inode block, varied indirect blocks, or the data block itself. Further, we designed specialized data structures to keep track of data and free space in the storage devices. By leveraging the fact that data are often inserted in temporal order, we can minimize metadata to the point that it can be easily kept in main memory.

In our system, a data insertion is translated into only one disk access, which allows customized indexes for data retrieval. Our design can aggregate local and remote main memory and SSD to enable most metadata lookups to happen in the types of memory that support random access. We can also exploit remote direct memory access to utilize remote RAM and SSD efficiently. We also prototyped major features of our real-time middleware system. Note that our system leverages Linux buffer cache and caches on computer disk devices to achieve performance. In preliminary tests, our system can achieve several orders of magnitude performance improvements over traditional systems. Moreover, performance is predictable and consistent, which is crucial for real-time data ingestion.



Performance evaluation of GridMW and MySQL, ingesting a large number of PMU data records.

This project produced several papers and presentations describing the design and initial implementation of our real time data middleware system. Additionally, our work led to client funding for managing power grid data. In FY 2012, we plan to leverage solid-state devices. We will implement a distributable version of our system that can utilize parallelism, improve performance.

Signature Discovery Analytic Framework

Adam S. Wynne, Yan Liu

◆ The creation of next-generation signature detection capabilities requires a signature development platform that provides advanced tools and services to discover, verify, and exploit complex threat signatures in multiple heterogeneous data sources. This project will create a software architecture that integrates novel and existing data analysis algorithms into a single, enterprise-strength software system that leads users through a methodology of systematic signature discovery across multiple domains. ◆

Software tools and infrastructures for the discovery of domain-specific signatures are in use and well known, but none has the flexibility and reusable methodology required to be extended to multiple domains. These tools are typically applied ad-hoc for the task at hand or are integrated using workflow software, which provides a graphical interface to integrate disparate software tools. In either case, methodology is not made explicit in that it is tied to a particular scientific domain or not documented systematically. This makes it difficult for signature development tasks to be repeated and applied in other contexts. Further, although the workflow tools help to automate and integrate distributed computing resources, they are often challenging to apply in practice and cannot individually take advantage of high-performance computing resources that are required to solve many of these problems. To build a system that enables users to employ a fundamentally new methodology, we are conducting a literature review on current signature development practices, and we are learning about the generic tasks that a signature analyst must perform and the algorithms that must be used, regardless of domain. To support the execution of these tasks, we are also conducting research on software architectures and model-driven software engineering techniques that can be used for partially automated workflow creation.

The objective of this project is to create a novel software architecture that combines a rigorous signature development methodology (developed under another research task) with highly flexible, robust software architecture and associated tools. Thus, this project will result in a lasting software toolset that can be used to develop signatures in a wide variety of domains. This will help achieve the central goals of the initiative by reducing trial and error, allowing users to reuse existing tools and approaches, and providing a reproducible mechanism for constructing and evaluating signatures. In order to accomplish this, we focused primarily in FY 2011 on the discovery of requirements and use cases to drive the development of the analytic framework in later years. This effort was undertaken through meeting with project teams and reviewing the scientific literature on existing approaches to signature development. To achieve the project's scientific goals, we performed a literature review of scientific workflow tools to determine the state-of-the-art and the options for leveraging existing tools. In addition, we worked to update and improve the existing PNNL Middleware for Data Intensive Computing (MeDICi) software platform on which we will build the analytic framework so that it is ready for use in FY 2012.

We delivered an initial version of the Analytic Framework requirements and use case documents at mid-year and are preparing the final version for delivery. The use cases will serve two purposes: to drive the development of analytic framework features and to serve as templates to generate automatically partial workflows for a given task. Developing use cases also led to the early stages of architecture design. Our general approach is to design and document architecture elements incrementally as framework requirements and use cases are clear enough to do so. As a result, we have created the initial version of component interfaces for some of the more well-developed use cases.

Our conclusion is that the Analytic Framework architecture must be built to extend the capabilities of an existing tool. These extensions will include the use of a robust and highly flexible integration layer (enabled by MeDICi), the addition of semantic features for the recording of provenance and representation of data types, as well as the creation of a semi-automated workflow generation capability.

In FY 2012, we will continue to develop use cases as integration scenarios become clearer and as new scenarios are added. We will begin to build software components iteratively around the use cases, culminating in small-scale demonstrations at the end of the year. Careful focus will be placed on designing interfaces between components so that the larger system is stable and well-engineered. We will also work closely to provide semantic algorithms used to perform advanced task and workflow matching needed by the analytic framework. Specifically, we will define integration points and deliverables for this project so that the tools developed can be integrated efficiently into the overall framework.

Signature Quality Metrics

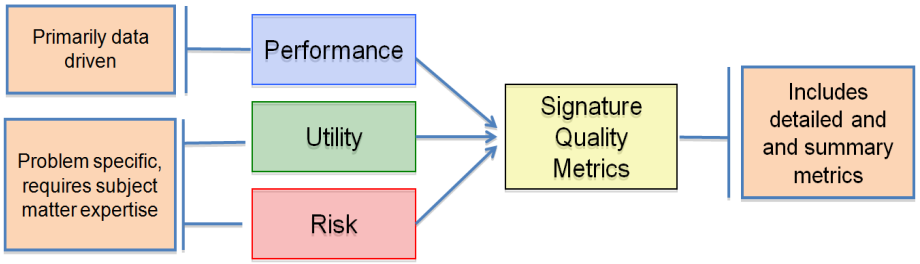
Landon H. Sego, Stephen D. Unwin, Alan J. Brothers, Aimee E. Holmes, Mark R. Weimar, Richard M. Anderson, John A. Ramey II, Spencer E. Hays, Mark F. Tardiff

◆ Signatures that indicate or predict a phenomenon of interest are used by scientists in virtually every field of study. Our project addresses the need to assess the quality of these signatures by developing a calculus for examining the performance, costs, risks, and benefits associated with a given set of signatures—with the goal of identifying optimal signatures for a particular application. ◆

Extensive literature searches at PNNL have unequivocally confirmed that signature discovery and detection are exercised by many scientists the world over, working in many scientific disciplines and for many different purposes. Consequently, a domain-agnostic methodology for assessing the quality of signatures will help researchers ensure that signatures achieve their intended purposes. The need and significance of signature quality metrics (SQM) can be summed up by this well-known remark by Lord Kelvin: "If you cannot measure it, you cannot improve it."

To this end, there are numerous relatively mature methodologies that could contribute to measures of signature quality. Examples include measures of signature performance (e.g., false positive and false negative rates), cost/benefit analysis, risk analysis, decision science, and utility theory. Notwithstanding the varied approaches, we have not identified an attempt to holistically measure the quality of signatures in terms of performance, utility, and risk. Our approach is novel in that it involves a synthesis of existing assessment techniques, as well as the development of new approaches, to create a flexible methodology for measuring the quality of signatures. SQM will enable scientists to address the following types of questions: Is one signature better than another? Does it make sense to attempt to improve upon an existing signature by modifying that signature or even creating a new one? What can we do to improve the performance of a poor signature?

Our strategy for developing SQM has been to assemble a team of experts with diverse backgrounds, including statistics, economics, psychology, operations research, risk analysis, and decision analysis. Drawing on this diversity of perspectives and experiences, we are developing a systematic approach for measuring signature quality and then demonstrating the methodology in the context of actual signature discovery efforts. Specifically during FY 2011, we completed an initial literature search and developed a first draft of the SQM approach in terms of performance, utility, and risk. Performance refers to how well the signature correlates to the phenomenon of interest. Utility represents the value of problem-specific attributes, such as costs, time-to-decision, ease of use, etc. that are typically associated with the construction and deployment of the signature. Risk refers to the likelihood and consequences of decision errors that may result by employing the signature.



Components of the SQM methodology.

To ensure that our approach is useful to other scientists, we simultaneously investigated a variety of signature discovery efforts by engaging with researchers in a number of areas. We especially focused on three application areas: bioforensics, proteomics, and radiation portal monitoring. For the bioforensics area, we demonstrated our metrics of signature performance and utility for a Bayesian network designed to predict the culture media used to grow a microorganism. Our work resulted in identifying the set of laboratory tests that were most influential in correctly predicting the culture media. In proteomics, we submitted a conference paper that assesses the performance of clustering algorithms applied to microarray data, an important first step in assessing the quality of clustering used in the process of peptide identification. For radiation portal monitoring, we defined research objectives and obtained data necessary to compare the quality of various signature algorithms in detecting radioactive material at U.S. ports and border crossings.

Our research plan for FY 2012 has three components. First, we plan to conduct theoretical investigations to advance the state-of-the-art in assessing signature quality. In particular, we will address the challenge of how to measure the performance of a signature when there is no "gold standard," or ground truth. Second, we will continue to demonstrate and refine SQM in the context of the three aforementioned application areas, and possibly engaging a fourth. Finally, we will begin to develop software tools that will guide researchers in applying SQM to their own projects.

Single Node Optimizations for Extreme Scale Systems

Daniel G. Chavarría-Miranda, Khushbu Agarwal, Sutanay Choudhury

◆ This project is investigating the necessary design and implementation techniques to support efficient utilization of node resources for extreme scale scientific applications. We believe that the efficient utilization of node memory and processing elements will be principal factors in achieving the levels of scaling and performance required for exascale applications. ◆

Extreme scale systems will provide an unprecedented opportunity for scientists to attack larger and more complex problems and reach solutions dramatically faster. These new architectures promise to be qualitatively different from existing computers and extracting their full capabilities will require significant innovations in programming models and the underlying primitives used to implement them. The next generation of computers will be characterized by larger numbers of nodes, each with hundreds to thousands of cores. Although the collective capabilities of each node will be large, the resources available to individual cores will be much smaller. Resources will need to be shared to a much greater extent between processes than before, much higher levels of parallelism will need to be exploited by applications, and sophisticated scheduling will be required to avoid very limited bandwidth.

The outcomes of this project include the development of new optimization methods and techniques for computation on emerging extreme scale nodes; the integration of such capabilities with Global Arrays (GA) for system-wide scalability; and the demonstration at scale using a molecular dynamics driver application. Applications with communication-intensive execution patterns such as molecular dynamics can benefit even more when they can effectively exploit intra-node resources (shared memory, multicore processors, accelerators) to reduce their communication requirements. Careful assignment of logical tasks to multicore nodes to exploit data access locality is essential to reducing inter-node communication requirements for communication-intensive applications.

Most HPC applications have been developed using the Single Program-Multiple Data (SPMD) paradigm, which typically is realized by starting up a number of sequential processes (*0...p - 1*) on individual "processors" (cores in modern systems). Parallelism is typically realized *only* through this mechanism. Thus, this model can only implement explicit parallelism in a single level. SPMD models incur a high cost in data replication due to private per-process address spaces; this will no longer be feasible in the exascale era due to expected reductions in per-core available memory.

In FY 2011, we focused on three primary activities: design and implementation of a multithreaded extension to GA: *Global Futures*, development and performance analysis of multithreaded kernels for molecular science applications: two-electron contributions in the Self-Consistent Field method and force calculations in classical molecular dynamics, and the development and integration of schemes to decrease GA metadata overhead.

Global Futures is an execution model extension to Global Arrays, which enables locality directed, multithreaded execution on each GA process. The basic concept behind *Global Futures* is the idea of shipping computation to where GA data is located:

```
execute foo(a, b, c) on_home(g_a(1:10, 2:3))
```

In this example, the function called foo() will be executed on the process that owns the slice of GA instance corresponding to the subscripted reference. This function invocation on another process is called a *future execution*.

We prototyped the use of *Global Futures* for molecular science applications in the context of the Self-Consistent Field (SCF) calculation. Specifically, we converted the two-electron contribution (most time consuming part) to the Fock matrix build into a *Global Futures*-based computation, which involves a computationally sparse n^4 calculation over an n^2 data space. n^4 tasks are enumerated, and most of those tasks do not add any contribution to the Fock matrix (only a small percentage [< 1% for larger inputs] of tasks do). The traditional way this is implemented is with a counter-based approach, where GA processes grab the next task ID from the n^4 pool and inspect associated data for possible computation. This approach introduces quite a bit of communication and does not scale well to large process counts because it does not consider locality.

In the *Global Futures*-based implementation, we each process enumerated n^4/p tasks (where p is the number of processes), with each process inspecting only tasks for which the data are local. Other tasks are packaged into futures and sent to their home processes for checking. At the end of this phase, processes will have stored in local queues only tasks that do contribute to the Fock matrix build. However, the number of tasks per process will be highly unbalanced with respect to other processes. After this phase, tasks are redistributed to improve load balance at the cost of some locality. This "discovered" task schedule can be reused and preserved for the subsequent iterations of the overall SCF calculation. For execution, tasks are popped from the local process queue and executed using futures directed to the local

process. We executed this implementation on EMSL's Chinook on several thousand cores and observe very good scalability, compared to the naïve implementation using processes and a counter-based load-balancing scheme.

Additionally, we implemented a multithreaded OpenMP implementation of the force calculation for the next-generation ARGOS classical molecular dynamics package. ARGOS has two different routines for the force calculation: self-self interaction (particles from the same cell) and self-other interaction. Our results show that the OpenMP implementation is scaling well as we increase the number of cores. Finally, we implemented and prototyped a solution to decrease GA's metadata overhead by storing a global array instance's pointers to remote sections of the array in shared memory on each SMP node. This reduces the overhead by the number of GA process instances resident on each SMP node. This is a significant reduction in light of the increase in cores per node: NERSC's Hopper has 24 cores per node, compared to EMSL's Chinook with 8 cores per node.

In FY 2012, this project will focus on the following activities:

- Design and develop NUMA-aware memory allocation support for PGAS-based programming models.
- Design and prototype multithreaded execution models that take advantage of NUMA locality.
- Evaluate these developments in the context of the ARGOS molecular dynamics applications.
- Port the Global Futures framework to a new active message-based PGAS framework.

SoftShuffle: A Game Changer for Secure Software System Implementation

Mohamed Y. Eltoweissy

◆ This project designs and implements secure resilient software systems that exploits multiple, preferably independently developed implementations of system components to introduce implicit behavioral non-determinism and employs automated recovery from implementation flaws to enhance system resilience. SoftShuffle will induce a paradigm shift from today's software monoculture to attain security and resilience through diversity, shuffling and automated recovery. ◆

Developing secure, resilient software systems is challenged by implementation flaws that could lead to serious security vulnerabilities despite careful auditing and analysis of the software specifications. The implementation flaws are usually difficult to detect and fix before the system is operational due to the prohibitive cost of auditing the implementation or testing all possible inputs and system states. Anonymous intruders could exploit implementation flaws to gain partial or total control of the system, or cause the system to crash leading to undesirable downtime. To address this class of vulnerably, a novel approach for implementing mission-critical software systems is proposed. SoftShuffle can tolerate the existence of implementation flaws while considerably enhancing the security and resilience of the system. SoftShuffle decouples software specifications from system implementations and performs "hot" shuffle among a multiplicity of diverse implementations for the same specifications.

The primary objectives of SoftShuffle are to confuse the attacker by non-determinism through shuffling of software system component implementations, to improve the availability of the system by providing means to automatically recover from runtime flaws, and to enhance the software system by survival of the fittest through trust-based component selection in an online software component marketplace. SoftShuffle makes software systems moving targets, thus effectively transforming white boxes into "hardened" black boxes at runtime. As an added benefit, we envision the development of a new paradigm for software implementations. The goal is to produce software component architecture capable of maintaining the operational integrity of the whole system while allowing shuffling of different implementation variants. Specifically, SoftShuffle will provide a runtime environment that is resilient to attacks targeting software implementation flaws with a software development platform design that allows programmers to develop multiple alternate implementations of system components.

With SoftShuffle, we perceive a software system comprised of interconnected components that act and interact to achieve a desired functionality. Each component adheres to certain specifications defining its explicit behavior. At the same time, each component exhibits an inherent implicit behavior due to the potential individuality and variability across different execution environments and different implementations of the same specifications. Accordingly, we can classify the types of vulnerabilities of a software system into either specification or implementation. The latter vulnerability is much more difficult to detect because auditing the implementation requires greater effort than the specifications and is usually infeasible, especially for commercial, off-the-shelf components. It is also implementation dependent and almost unavoidable.

In FY 2011, we designed the SoftShuffle that is being incorporated in our cooperative autonomic resilient defense platform for cyber-physical systems, built a demo of the core engine, and designed and prototyped our automated recovery subsystem. We pioneered a biologically inspired active component architecture that is composable, online programmable, and intrinsically resilient. We successfully induced behavior non-determinism and developed a novel approach to measuring the amount of non-determinism in the system at any time. As a result of this project, we have published three peer-reviewed papers, presented at several conferences, and have been invited to a national workshop. We will continue refining the architecture and preliminary prototype, producing a quantitative evaluation of "Behavior Encryption;" a new concept through this work.

Plans for FY 2012 include extending the SoftShuffle prototype, simulation, and analytical model. We will refine the design and code. By introducing non-determinism of implicit behavior into the system and employing automated recovery, the effort of discovering and exploiting implementation vulnerabilities becomes futile. Further, continual enhancement in components is achieved by fostering an electronic marketplace for component implementations. To make sure our system is fully prepared, we will conduct rigorous evaluations both internally and using external red teams.

Synergistic Integration of Feature Recognition and Analysis for Chemical Imaging Data

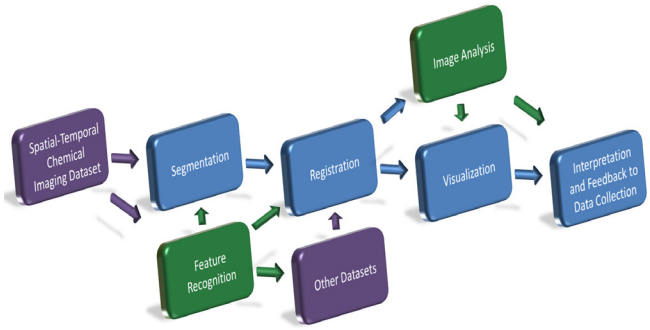
James P. Carson, Daniel R. Einstein

◆ The scientific challenges of today and the future are complex and generally require the integration of a multiple experimental results. This project is building the foundation for new and unique critical research capabilities in order to perform image analysis and feature recognition of very large spatial time-varying datasets. The immediate impact includes facilitating knowledge-discovery in the fields of soil remediation and renewable energy production. ◆

The ability to see both in time and space the molecular details of chemical processes is critical to future research in multiple areas of national interest, including energy production and utilization. Developing new instrumentation and integrating information from multiple data sources is an important step in achieving such new capabilities. Generally, there is a need to make existing feature recognition algorithms accessible to scientists and to customize such approaches to the particular needs of the specific data collection instruments and feature types. Currently, tools and techniques are being developed to image chemicals, materials, and biological molecules at resolutions ranging down to nanometer scale.

This project was initiated to establish new capabilities that allow scientist-driven interactive feature recognition and analysis for their chemical imaging-based data. The goal is to develop a toolkit with feature recognition algorithms integrated and customizable to specific chemical imaging acquisition protocols to make new analysis possible and provide more direct feedback to researchers during the image acquisition process. The toolkit will be integrated into an image handling framework spanning from data acquisition to final results interpretation. This will allow the tools to augment positively data processing steps such as segmentation, image-to-image registration, and data visualization/interpretation.

In FY 2011, we initiated a discovery process to identify specific needs and skills in feature recognition and analysis for chemical imaging research. We created a prototype tool with graphical user interfaces to allow interactive feedback to chemical imaging scientists. We applied this capability to two chemical imaging LDRD projects. The first was an effort that developed spatial imaging using soft ionization mass spectrometry for complex systems. Scientists developing this new imaging technology lacked real-time feedback during multi-hour experiments, having to wait until the conclusion to process data and view results. To address this need, we developed a tool that allows spatial and spectral features of data to be visualized and analyzed as they are collected during the experiment. This enhances the development and application of instrument technology by creating the possibility to adjust the instrument during the experiment interactively or restart a failed experiment prior to completion.



The interactive role of feature recognition and image analysis on the multimodal integration framework for chemical imaging analysis.

The second effort was one investigating microbial biofilm structure and function data by correlating volumetric images collected from multiple imaging modalities, including electron microscopes and beam-lines. Allocated time on these instruments is limited, thus making it important to receive feedback on data quality as quickly as possible. Adjustments to the experiment can be implemented while access to the instrument is still available, but only if one can see what adjustments need to be made. We developed a prototype portable tool allowing the visualization of spatial features in volumetric data. This tool currently includes customized image processing filters that highlight the features of interest in this specific data.

Our feature recognition tools are modular and expansible, enabling their application to a variety of other chemical imaging projects. In FY 2012, the feature recognition toolkit will be refined to increase utility of the toolkit and increase capability for chemical imaging research. We will also incorporate new objectives in the field of heterogeneous catalysis analysis. This work will develop a test based on features stored in a quality database that will determine if catalysis image data are unsuitable for analysis. These future project milestones will make significant contributions to chemical image analysis capabilities by providing faster and more accurate feedback to researchers conducting imaging experiments.

The Analysis and Discovery of Influencing Factors in Social Media

Michelle L. Gregory, Eric J. Marshall, Andrew J. Cowell, Liam R. McGrath, Eric B. Bell

◆ The specific focus of this work is on building algorithms and methods that can aid in identifying how information flows through social media sources and how influence is exerted within social groups or networks. ◆

There is a rich history of text analytics tools and methods that enable the analysis and understanding of large collections of text. In the last 25 years, algorithms were not developed to be used with the unique characteristics of today's social media data. With the emergence of new media types such as blogs, Twitter, and other social media sites, reaction to news or events is instantaneous, often well before traditional media sites can digest and produce their own stories. Data from these social media can be extremely useful in identifying the opinion drivers within a community. The ability to identify influential people or opinion leaders is paramount to the success of any mission that attempts to understand events unfolding through social media (such as the Arab Spring) or influence the outcomes of events.

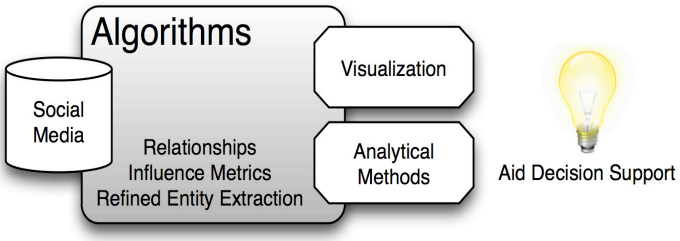
The aspects of social media that make it difficult to handle by traditional text analytics are that it is usually messy, sparse data, not content-rich like single source news articles. Often, lexical items are introduced and unconventional shorthand is commonplace (e.g., IMHO for "in my humble opinion" in texting). In addition, the conversational nature of social media makes it very difficult to track topics and entities. However, the major shift to the use of this data makes it the new place to get information for political news, health services, scientific fields, and intelligence gathering. New text analytics algorithms need to be developed to handle these data types.

In particular, data types have facets of information not found in traditional text types; they carry information about the relationship between users. New algorithms need to be developed to isolate these sorts of information from social media as well. We illustrate that the process of social media analytics is very similar to text analytics in general, but that new algorithms need to be developed to handle the data structure as well as make use of the distinct information provided in these data types. The scientific innovation of this work lies in addressing this research gap. Through our research, we developed algorithms and methods to glean information from social media sources. Specifically, we developed algorithms and methods to determine how information flows through blogs in order to identify influential sources. As part of this effort, we created novel methods for harvesting social media data and identifying groups through which information flows, but who are no specifically linked. This project has had impact both in scientific breakthroughs as well as establishing the researchers as leaders in this technical area.

In FY 2010, we developed a mathematical proof that combines our metrics of influence into a single metric. This has been extremely useful and has received positive reviews. Additionally, we were able to build an early prototype for blog searches and harvesting. While the concept and outline was developed and the methods defined, we incorporated machine learning methods into our harvesting capabilities during FY 2011. This effort resulted in a publication .

To identify the best data for use in developing our influence methods, in FY 2011 we realized that we needed to be able to define groups within a dataset to focus our analysis. The assumption was that "non-real" groups tend not to be influential. Therefore, a large part of our effort was to identify and characterize groups within the data. The goal was to compare groups, or members of groups, and identify those members that do not fit (i.e., "non-real" groups). To test the grouping capability of these algorithms, a non-translated Russian dataset was analyzed. The dataset contained Russian blogs in which some blog authors belong to a single abstract group and some do not. The results show that we were correct in placing members within groups in our test set as well as placing seven out of the nine authors in the Russian data into the correct group. This effort resulted in two conference papers and one journal article.

Through this project, we have been able to develop novel social media harvesting and grouping algorithms that have enabled us to test our influence algorithms. These efforts have led to a total of five publications, including an outstanding paper award at an international conference.



Text analytics for social media.

Visualizing Uncertainty in Conceptual and Numerical Models for Geological Sequestration

Luke J. Gosink, Mark D. White, Diana H. Bacon, Bruce J. Palmer, Landon H. Sego

◆ This research will help scientists characterize and quantify uncertainty in the conceptual and numerical ensembles that are commonly used to assess the viability and long-term impacts of sequestering carbon dioxide at select geological regions. ◆

Despite being actively researched for several decades, the field of uncertainty quantification (UQ) is still rapidly evolving and developing. Existing UQ research attempts to quantify the uncertainty in a given system based on the system's reliance on instrumentation (used to obtain ground truth), conceptual modeling structures (the mathematical and domain-specific models used to create a system that can predict and simulate a real-life event), and numerical approximations (the methods used to approximate the operation of the system). A fundamental challenge to assessing uncertainty and accuracy in sequestration models arises from the fact that ground truth data – essential for most UQ and risk analysis tasks – is largely unavailable; in many cases reliable, sufficient subsurface ground-truth is too costly or infeasible to obtain.

Our objective is to address the above challenge by developing novel methods for characterizing uncertainty that can be used in the presence of minimal ground truth measurements. We combine the analytical strengths of statistics with the interactive power of scientific visualization and visual analytic methods. This approach addresses uncertainty through the comparative analysis of varying scenarios, considering all likely events predicted by numerous systems (i.e., varying conceptual and numerical models) for a fixed sequestration site. Our integrated approach is novel in the geological sequestration, visualization, and uncertainty quantification communities. As an integrated component of the Geological Sequestration Software Suite (GS^3), this project supports risk analysis, management, and mitigation tasks for sequestration activities through a unique combination of techniques derived from the fields of statistical analysis, scientific visualization, and visual analytics. Our work will ultimately allow scientists to advance the understanding of sequestration modeling and more accurately assess the performance of and long-term impacts to sequestration activities at potential reservoirs.

Our work during FY 2010 focused on three stages: identifying aspects of uncertainty to address within GS^3, identifying viable strategies to address these uncertainties, and acquiring data for testing and validating our strategies. Initially, we identified the varying sources of uncertainty present in each of the existing projects supporting GS^3. We collaborated and consulted with other projects and identified both elements of uncertainty and potential strategies for detecting and characterizing these uncertainties. Ultimately, we identified uncertainty to address in two stages of GS^3's modeling framework: its conceptual and numerical model development stages.

In FY 2011, we completed three significant stages of the project. First, we completed the construction of our statistical analysis framework for performing UQ. This framework is based on a Bayesian approach that combines ground truth observations (i.e., monitoring data) with the predictions obtained through an ensemble of conceptual and numerical models. The framework facilitates UQ analysis for both the ensemble and its constituents by providing a mechanism for identifying and quantifying the spatial, parametric, and temporal regions where uncertainty and model errors are greatest. This analysis further supports a means for performing direct model-to-model comparisons and model ranking. From this ranking, we can identify which models in the ensemble are most and least accurate.

In our second area of work, we completed a field study that helped verify the accuracy and utility of our statistical framework. This study, which will appear in a forthcoming publication, examines two separate field experiments that monitor and attempt to predict the behavior of two separate subsurface events concerning the transport of chemical species. Through our framework, we helped accurately quantify the uncertainty in each experiment's conceptual and numerical ensemble and identified which models in the ensemble were most accurate.

Finally, we have extended this statistical framework with a preliminary suit of scientific visualization software tools. These tools, which are working prototypes for this project's eventual application deliverable, help to convey the information generated from our statistical framework in a more meaningful way by visually conveying (through isocontours and surfaces, scatterplots, and time series displays) where model uncertainties are greatest.

In FY 2012, we will focus on three tasks. We will continue validating our statistical framework with further field studies. We will also complete the development of our visualization application that will become the interface to our statistical framework. Finally, we will integrate this tool into the GS^3 environment so that it is widely accessible for all GS^3 clients.

Vulcan: Unexpressed Communication

Michelle L. Gregory, Joseph R. Bruce, Glenn A. Fink

◆ The aim of this research is to create a secure, privacy enhanced collaborative environment for computer security professionals whose data sensitivities make sharing via normal means infeasible. Our work has enabled the rapid coordination of cyber defenders without interrupting their workflow through enabling situational awareness of streaming social media data and automatically capturing analysts' informational queries and pushing those to other users. ◆

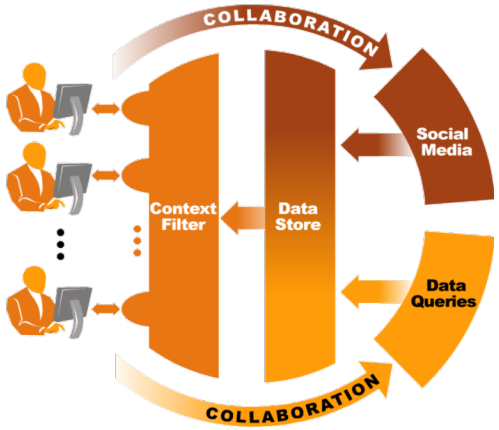
Sharing information is necessary for effective collaboration. In the post-September 11 world, government agencies have changed approach from a "need-to-know" mindset to "need-to-share" information. Cyber security problems are often far-reaching global affairs that cannot be understood easily. However, sharing introduces potential security and privacy problems, and sharing information takes work, both to share and use the information. Simply automating the sharing process can exacerbate security issues. Cyber defenders need a way to share information with outside organizations, governments, and countries without divulging sensitive or proprietary information and without revealing their own identities.

The Vulcan collaboration system tracks activities of cyber analysts as they go about their work. As long as they stay within tracked window(s), queries to internal data and external information sources are recorded and passed to other Vulcan users. Users are never identified, but aggregate information can help cyber analysts decide more effectively avenues for further investigation based on others' actions. The Vulcan prototype compares internal data queries of its user base for similarity and uses this information as a recommendation system to propose related query terms. Additionally, the prototype gathers Internet information sources by its constituency and tracks actual information usage to determine trends and suggest additional sources to users.

Our aim is to produce a system capable of enabling collaboration across these boundaries while preserving the private nature of an analyst's identity and skill set. The system will be fully automated, analyzing sources and queries employed when exploring data, and communicating the analysis. This has the effect of not only enabling collaboration without added input but also makes possible the anonymity analysts need and protects sensitive information. Benefits to individual analysts are targeted source content, where sources can influence information exposure; situational awareness, where queries can trigger a response from the observing analyst; and knowledge sharing, where analysts improve skills through cooperation and trust-based relationships.

During FY 2010, we studied collaboration habits and cyber security analyst needs, defined an architecture for the collaboration system, and built prototypes and some code base. We conducted interviews concerning analysts' use of social media sources and how information informs daily workflow. Accomplishments during FY 2010 included publishing a journal article on cyber analyst processes. We wrote another paper on our experiment at the PRCCDC that was designed to determine metrics to help measure the effectiveness of a collaboration treatment such as Vulcan. We also used in situ situational queries as a measure of team awareness and found that there is a relationship between the time and accuracy of a team's answers and its ultimate score.

Armed with knowledge of cyber analysts' workflow and information gathering processes, we were able in FY 2011 to focus on building prototype systems that enable ambient collaboration. We focused heavily on client engagement in and worked with analysts from NTOC's V2 organization. Within the emerging threats group we were able to isolate a group of analysts who rely heavily on a single technology, Wireshark, to conduct investigative queries. We built automatic methods to track the queries of each user in Wireshark and insert the user footprint information into the Wireshark backend so any other user can see if information returned from the query has been viewed by another analyst. We also built a couple social media prototype systems that take real-time streaming input from blogs, twitter, and cert reports and are viewed in a single information space for situational awareness.



Vulcan provides automatic collaboration using two sources of data: queries into internal data and accesses of Internet information such as social media.

We secured client funding to continue this work in FY 2012.

Nuclear Science and Engineering

A Virtual Testing Toolbox for Predicting the Properties and Behavior of Multiphase Materials in Disposal Environments

Joseph V. Ryan, Anderson L. Ward

◆ This project is developing a virtual testing toolbox with capabilities for identifying and determining values for critical modeling parameters needed for the long-term prediction of waste system performance that meets regulatory criteria. Novel experimental techniques will also be developed to advance the science of multiphase interactions. ◆

The safe immobilization of nuclear waste is of critical importance to all U.S. citizens, whether the waste is a legacy of weapon development or the result of peaceful power generation. This project aims to produce a process whereby the critical properties of the most complex (multiphase) waste forms can be systematically identified, determined, and incorporated into modular algorithms that fit seamlessly into continuum transport models. Achieving these objectives will increase confidence in performance predictions and will naturally result in a large reduction in the costs required for disposal, inspection, and maintenance of multiphase waste forms.

Every waste form system is inherently multiphase. Even nominally homogeneous materials such as waste glasses become multiphase problems when incorporated in a system (canister, fill material, etc.) or when corroded by water (amorphous gel layer, crystalline corrosion products, etc.). Many of the existing prediction algorithms, however, assume a relatively physically homogeneous source term. The difficulty of modeling complex phenomena such as the evolution and degradation of a waste form system originates in the underconstrained nature of the interactions. The particular system of interest contains several classes of parameters:

Geometries, including pores, surfaces, interfaces between materials/phases, and the spatial arrangement of and relationship between the various phases.

Materials and phases, e.g., glass evolves into a system composed of bulk glass, surface alteration layers, near-field soil environment, and associated interfaces, where most (if not all) chemistries and compounds change from the original state. Similar processes occur for nearly every waste form material.

Kinetics, where reaction rate constants describing the temporal evolution of a material into a new phase, the creation of interfaces between phases, and the diffusivities of assorted molecules through various phases.

Time, as "critical time" benchmarks progress toward a totally dissolved end state, such as time when concentration of a radionuclide in the near field at a given distance from the waste form surface reaches 50% of its asymptotic value.

Commonly used in a wide range of fields, inverse modeling methods help define experimental needs for parameterized data. These methods use "merit functions" (such as measured corrosion rates) while searching for parameter combinations that minimize the error between the predicted and observed behavior at a given time. Constraints are used to keep possible answers within the realm of reality. For waste form degradation, these include known limits for geometries (e.g., layer thickness or porosity), diffusivities, reactivities, phases, and phase interfaces. However, existing data in these areas are incomplete and result in the utilization of useful but insufficiently constrained parameters for a discrete solution to the inverse problem. By identifying gaps, experimental work can be targeted to reduce uncertainty in model parameters.

The objective of this work is to develop a Virtual Waste form Testing Toolbox (VWTT) to provide the technology needed to reduce the number of physical/laboratory tests required to produce constrained parameters quickly and efficiently to assess product quality and long-term degradation mechanisms of multiphase waste forms and other multiphase materials in disposal environments.

For our first task, some existing waste forms have a large quantity of existing structural data, but competing algorithms for determining performance. This is particularly the case for glass dissolution, where the initial rate laws become much more complex once corrosion progress presents a multiphase system. To gain insight on which mechanistic models are appropriate, we focused in this task on evaluating existing models using inverse modeling techniques and data available in the literature. The inverse modeling, performed using the PEST code, determined the best fit combination of parameters through regression analyses, and then gave estimates of the sensitivity of each parameter.

The development of inverse modeling as a tool for the evaluation of multiphase waste form degradation models was very successful. Developed by the French atomic energy commission (CEA), the GRAAL model calculates the dissolution of glass as a diffusion control process. Through our analyses, we found that two of the six parameters (the precipitation rate of crystalline alteration phases and the surface dissolution rate in pure water) are hyper sensitive, essentially determining the model result. Even more importantly, two other parameters (the release rate of boron & alkalis and the diffusion coefficient of water through the transport barrier layer) appeared to be completely non-

sensitive. This has generated considerable interest in the international community, leading to a DOE/CEA collaboration to optimize GRAAL to provide a more appropriate parameterization, and then to apply these techniques to recent modifications of the code. This work has now been picked up by programmatic funding and will be continued (and expanded) using those resources.

A finite difference code developed at PNNL was also evaluated, and the model parameters were reasonably evenly sensitive with none driving the model results to an unreasonable extent. Unfortunately, the model was also found to be computationally stiff, requiring high computational power. Both models were found to have serious problems handing the complexity of the multiphase material formed during degradation, and a need was determined for a glass degradation model that uses a finite basis set of chemical reactions to predict formation of the observed structures and their transport properties.

For this initial task in FY 2012, we aim to develop modeling tools that incorporate glass and mineral chemistries of the equilibrium and kinetic data bases (e.g., PHREEQC) into the more applicable computational fluid dynamics transport codes. Critical to this approach is to develop relationships that make use of the extensive experimental data to relate chemical composition to structure and transport coefficients such as the individual species diffusivities. We will continue to use inverse techniques that allow experimental data to be related to model parameters. We seek model parameters such as the basis set of chemical reactions, their associated chemical equilibrium and kinetic parameters, and species diffusivities that are invariant over all time domains and explicitly relate to knowledge of chemical composition and structure.

In the project's second task, cementitious multiphase waste forms (e.g., cast stone, salt stone) are shown to be viable candidates for immobilizing secondary wastes. These materials are chemically and structurally complex consisting of a heterogeneous mix of mineral phases of crystalline and amorphous material. The addition of secondary waste into cementitious materials complicates the relatively well understood evolution of cements, making long-term performance of the waste form problematic to calculate accurately. Several parameterization deficiencies were quickly identified for the system, including pore geometry, phase assemblage, and microstructure. Coordinated experimental characterization was performed to obtain values for these parameters. The loading of the simulated secondary waste solutions resulted in a variety of phase compositions and pore size distributions throughout the evaluation period. The setting reactions of cast stone after casting were also used to provide an evolving structure for analysis, mimicking in reverse the structure changes expected in degradation. The team successfully evaluated these changes in microstructure for the cast stone material.

One critical parameter for degradation models is the overall pore geometry. Utilizing a suite of techniques, the pore size distribution and overall pore volume were determined for all samples. The samples possessed pore volumes at all length scales, from nanoscale interstitial space probed with nitrogen adsorption to macroscopic trapped air bubbles observed with x-ray tomography. These accurate data will enable fluid transport models to predict more accurately the access of dissolving fluid to the radionuclides immobilized in the material. Knowing the access of water, it was then important to evaluate the structures in contact with the fluid. The overall volume of the crystalline portions of the microstructure was obtained by quantitative x-ray diffraction analysis. The volume percent of amorphous phases was also inferred with this method. The aspect ratio and potential surface area of these phases were explored through analytical scanning electron microscopy techniques, including wavelength dispersive and energy dispersive spectroscopies. Phase mapping techniques, coupled with phase identification gave a full picture of the microstructure of these materials.

The atomic bonding of the phases within the multiphase waste form also has an important impact on the reaction of the materials with water. For this reason, the chemical state and coordination of the constituent atoms were probed with nuclear magnetic resonance. These data showed the dominant and evolving structures of the material and which of them were accessible to pore water. This information is critical to the accurate modeling of phase dissolution, particularly for amorphous phases, where accurate analogue materials are scarce in equilibrium databases.

A novel technique for monitoring the changing structure was also developed. Impedance spectroscopy (IS) was shown to be highly sensitive to changes in the cast stone composition, pore geometry, and microstructure. Considering the dramatic spectral response to complex reactions and phase transitions cast stone endures during the curing process, a strong potential exists for IS to monitor the degradation of waste forms in situ. Although the complex impedance spectra observed could not be fit using a classical Cole-Cole model, data collected about the microstructures evaluated using this technique should enable future development of structure-response models for this powerful tool. Once models are in place, the potential exists for a rapid, non-destructive method that results in bounded parameters critical for dissolution models.

FY 2012 will see the publication of at least three papers from this work. In addition, we plan to incorporate these more detailed datasets into continuum geochemical reaction and flow models. In addition, the cross disciplinary team that worked together to parameterize this material quickly is available for similar attention to other complex, evolving multiphase systems.

Adaptation of Existing Probabilistic Risk Assessments to Support Reactor Aging Management

Stephen D. Unwin, Peter P. Lowry

◆ The intent of this project is for methodological advances to contribute to the evolving bases for identifying effective proactive monitoring and maintenance strategies in reactor aging management and setting materials research priorities. ◆

The extension of nuclear power plant operating licenses beyond 60 years in the United States will be necessary if we are to meet national energy needs while addressing the issues of carbon and climate. Probabilistic risk assessment (PRA) methodology has provided the principal basis for risk-informed decision-making in the nuclear power industry, yet limitations in conventional PRA methods constrain their value as effective tools in addressing aging effects and quantifying the risk and reliability impacts of aging management strategies.

The objective of this project was to establish a process for expanding the scope and underlying models of an existing PRA study to allow reactor aging issues to be addressed and alternative aging management strategies evaluated and compared. Principal challenges have been to model age-dependent equipment failure rates and to include in PRA models certain classes of components (mainly passives) that have not traditionally been captured in PRA studies. This latter challenge is critical because it is passive components (often not easily amenable to refurbishment or replacement) that may govern the accident and operational risks associated with an aging fleet of nuclear power plants.

This project has had four significant accomplishments: 1) establishment and demonstration of a systematic method for screening passive components and associated aging degradation mechanisms to determine which could significantly influence operating risk in an aging reactor (FY 2009), 2) introduction of a new class of risk importance measures that assess the contributions of components and degradation mechanisms to the rate of change of risk in aging reactors (FY 2010), 3) development of a Bayesian methodology for synthesizing materials degradation metrics with plant service data to estimate age-dependent component failure rates (FY 2011), and 4) establishment of the basis for adapting a PRA model to incorporate age-dependent component reliability models (all three fiscal years).

The quantitative models developed in this project (importance measures and age-dependent failure rates) drew on materials degradation information generated under the U.S. Nuclear Regulatory Commission (NRC) Proactive Materials Degradation Assessment (PMDA) Program. This is a large and expanding resource of expert-elicited information on the susceptibilities of nuclear power plant component materials to numerous degradation mechanisms. The methodology base developed under this project significantly increases the value and application scope of PMDA data by allowing it to be interpreted and utilized in a risk-based setting.

Specifically in FY 2011, the focus of the project was on development of a Bayesian methodology in which *prior* information associated with the failure rate of a component via a given degradation mechanism is provided by PMDA data. This prior information is then updated in light of relevant plant service data to produce *posterior* probability distributions over component failure rates. The methodology was demonstrated through application to stress corrosion cracking of dissimilar metal welds in PWR vessel head penetrations. Service data from 23 nuclear power plants made available by the Electric Power Research Institute was used to perform the Bayesian updates. The resultant probability distributions were then integrated into a PRA model to predict the typical impact on core damage frequency of the degrading components over the remaining plant lifetime. With the combination of component aging screening processes, new importance measures on aging risk, and Bayesian methods for estimating age-dependent failure rates, substantial progress has been made under this project in adapting PRA models to support development of risk-informed reactor aging management strategy and materials research prioritization.

The project produced nine peer-reviewed publications (7 published, 2 currently under consideration) and technical presentations at six international conferences in addition to other DOE/NRC/Industry forums. It has also allowed PNNL to establish a significant role in the Risk-Informed Safety Margin Characterization Pathway of the DOE's Light Water Reactor Sustainability Program, under which concepts initiated in the LDRD project were further developed. There was the additional opportunity to engage two new hires in the project.

This project was designed to provide the technical means of making sure that operational and regulatory decision-making on reactor life extension is properly risk-informed. Now complete, the project established processes for identifying those component aging issues that have the greatest influence on future risk and has produced methods for quantifying the risk-impact of degrading materials.

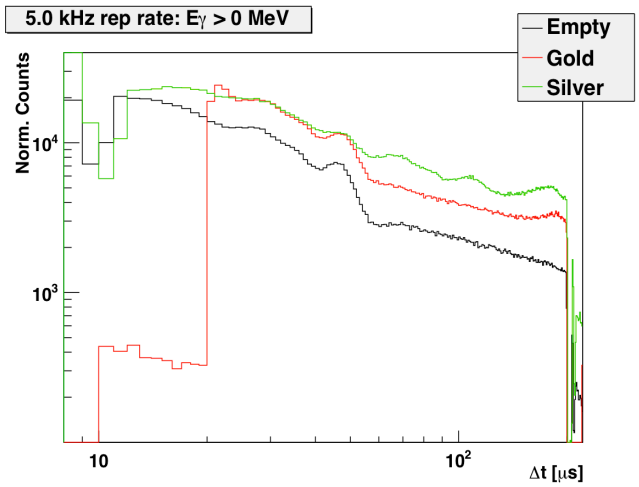
Advanced Nondestructive Assay for Safeguards

Glen A. Warren, Christopher J. Gesh, Sean C. Stave, Emily K. Mac, Benjamin S. McDonald

◆ This project is aimed at expanding the science base of direct measurement of uranium and plutonium isotopes in spent nuclear fuel and fresh mixed-oxide fuel. Lead slowing-down spectroscopy (LSDS) will be studied as a means to improve material accountancy for international safeguards. ◆

Accurate, non-destructive measurements of the plutonium content in spent fuel assemblies is a well documented but still an unmet challenge in international safeguards. As nuclear fuel cycles propagate around the globe, the need for improved fuel accounting techniques for spent light-water reactor fuel and fresh mixed-oxide fuel will only increase (e.g., for verification at interim or permanent storage or at the head end of a reprocessing plant). Current methods for estimating plutonium mass are based on the detection of signatures from non-plutonium isotopes, which are then coupled to computational predictions to infer plutonium mass in the assembly. A nondestructive assay technology that could provide timely (tens of minutes), independent (no operator-declared information), and direct measurement of plutonium mass with high accuracy would be a significant step toward both real-time accountancy and the prevention of materials diversion.

This project is aimed at expanding the science base of direct measurement of uranium and plutonium isotopes in spent nuclear fuel and fresh mixed-oxide fuel. The foundational assay method will be lead slowing-down spectroscopy and we will study that application as a means to improve material accountancy, but high-energy delayed gamma spectroscopy and combinations thereof will also be examined. Both techniques have shown promise in proof-of-principle theoretical and simulation studies but require additional theoretical study coupled to empirical validation. To conduct that empirical validation, we will perform the following tasks: 1) design, build, and characterize a lead slowing-down spectroscopy instrument; 2) develop and use the capabilities to design, fabricate, and characterize the specialized fission chambers required by lead slowing-down spectroscopy; 3) perform benchmarking measurements; and 4) develop and test analysis methods that address the complexities of neutron and gamma-ray self-shielding. This system will be used to study critical physics issues and to test instrumentation and data acquisition methods to develop non-destructive assay of spent fuel.



Time spectra from (n,γ) measurements with no foil (Empty) and gold and silver foils. For the gold foil measurement, the scintillator was vetoed for the first 20 μs.

Our primary focus for FY 2010 was the design and construction of the LSDS. The principle components of the instrument were a large cube of lead 1.5 m on a side with a neutron generator, a measurement sample, and detector instrumentation. The size of the lead cube was optimized for cost and measurement efficiency. The lead is naturally occurring and of high purity, which is important for maximizing the energy resolution of the system. While samples demonstrated a response when exposed to gamma rays, preliminary measurements using a neutron source showed no obvious fast neutron response.

The installation of the LSDS was completed in early FY 2011. The LSDS is part of the RDNS Active Interrogation Laboratory. To minimize room return (neutrons escaping out of the lead cube, bouncing off the walls, and returning to the cube), a thin layer of cadmium is placed around the cube. A layer of aluminum is placed outside of the cadmium to reduce the possibility of coming into contact with the cadmium. The existing Thermo Scientific P385 D-T neutron generator was used as the source of neutrons. The available time structure of the neutron beam is less-than-optimal for the LSDS measurements, but it provided an adequate neutron beam to conduct initial tests with the LSDS.

There are two aspects to characterizing the LSDS. First, one needs to understand the observed time-energy correlation for neutrons. Second, one needs to understand the flux of the neutrons as a function of the slowing time. The time-energy correlations can be measured by conducting (n,γ) measurements using selected foils that have strong, isolated resonances at specific neutron energies. Such measurements were completed using gold and silver foils. The time-spectra are shown in the figure. The structure in the empty target run around 50 μs is due to resonances in the germanium of the

BGO detector. The peaks above 60 μs in the gold and silver measurements are due to resonances in those materials. The neutron flux in the LSDS was measured by activating two groups of small foils, one covered in cadmium to reduce the influence of thermal neutrons and one without cadmium. Gamma spectroscopy was performed on those samples to determine the level of activation. Analysis to determine the flux is in progress.

Significant effort went into understanding the performance of the LSDS using the radiation transport modeling code MCNP. A large variety of issues were studied including the impact of room return, optimization of shielding, variation of flux with location in vertical hole, predictions for the (n,γ) measurements, and precision modeling of the neutron flux.

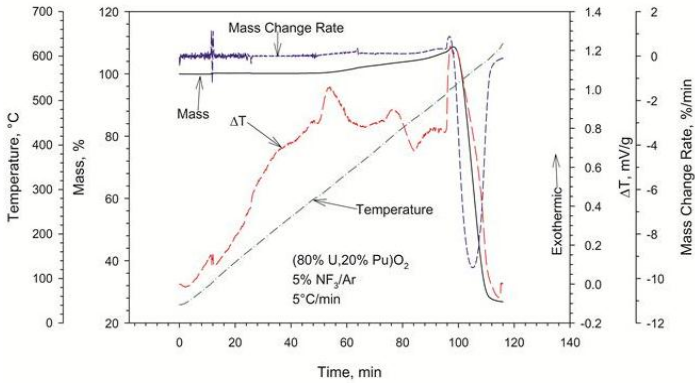
Activities in FY 2012 will focus on completing the characterization of the neutron flux and energy-time correlation and conducting a demonstration measurement with a ~100 g HEU sample. A series of (n,γ) measurements will be conducted to measure the energy-time correlation and width. Techniques will be developed to monitor the neutron flux in the detector, most likely using fission chambers. Measurements will be conducted using a fast neutron sensor and a ~100 g HEU sample to demonstrate the capability of the LSDS.

Application of Nitrogen Trifluoride (NF_3) to the Nuclear Fuel Cycle

Randall D. Scheele, Bruce K. McNamara, Andrew M. Casella

◆ Using NF_3 as a fluorinating agent offers the promise of a less hazardous process with the potential for using temperature as another tool to effect separations of fission products and transuranics from uranium, thus providing a new and more attractive fuels reprocessing approach. ◆

Actinide and fission product fluoride volatility have long been considered as a potentially compact, efficient approach for recovering valuable fuel constituents from spent nuclear fuels. Previous investigations found that NF_3 was an effective thermally sensitive fluorinating agent for uranium and technetium deposits in the Portsmouth gaseous diffusion enrichment cascade. NF_3 converted the uranyl fluoride and various technetium compounds to volatile fluorides. These results indicated that NF_3 could be an effective fluorinating agent for producing volatile fluorides from used nuclear fuel constituents at different temperatures thus providing a tool for separating and recovering valuable constituents.



Action of 5% NF_3 in argon on mixed (20% Pu,80%U)O_2 heated to 620°C at 5°C/ min as measured by differential thermal analysis (⊿T) and thermogravimetric analysis (Mass). ⊿T and Mass curves show uranium reacting exothermically near 300°C (60 min), producing uranyl fluoride before the uranium is converted to uranium hexafluoride and volatilized at 540°C (110 min). The differential of the thermogravimetric analysis (Mass Change Rate) further highlights this behavior. The plutonium is converted to non-volatile plutonium tetrafluoride as determined by x-ray diffraction powder pattern analysis. These analyses show that uranium can be quantitatively be separated from plutonium in an intimately mixed oxide.

Our objective was to determine whether NF_3 could be used to fluorinate and oxidize nuclear materials and fission products to recover and separate valuable nuclear fuel constituents based on differences in volatilization temperature as enhancement to traditional fluoride volatility fuels reprocessing flowsheets. Alternatively, it could be used in other applications for separations such as medical isotope recovery. Such uses would benefit from it being non-hazardous relative to molecular fluorine and hydrogen fluoride. The study strategy was to use thermoanalytical methods to study NF_3 thermal fluorination of uranium, plutonium, neptunium, and fission product metal, oxides, and fluorides.

Past years' studies showed that NF_3 effectively converts uranium metal, common oxides, and fluorides to volatile uranium hexafluoride. In FY 2009, we performed screenings using simultaneous thermogravimetric and differential thermal analysis to determine the thermal reaction sensitivity and mechanisms of the fluorination several oxides. For FY 2010, we completed preliminary studies on fluorination and/or oxidation of fission product oxides and investigated low-temperature fluorination/oxidation of uranium and plutonium metals to elucidate mechanism and kinetics.

In 2011, we investigated the fluorination of fission products that form and do not form volatile fluorides and investigated whether theoretical gas-solid reaction models could be used for NF_3 fluorination. In general, we found that thermal NF_3 will convert all oxides and metals of elements with volatile fluorides to volatile fluorides or oxyfluorides. We found that elements such as molybdenum and technetium will react and volatilize near 300°C compared with the 500°C required to fluorinate and volatilize uranium metal, the uranium oxides, and neptunium dioxide. As expected, we also found that NF_3 did not produce volatile fluorides or oxyfluorides from the lanthanides oxides, alkaline earths, and other transition metals that are not reported to form volatile fluorides or oxyfluorides.

Our reaction mechanisms and kinetics investigations found that found that isothermal results did not identically match reported theoretical chemical and physio-chemical fractional conversion reaction models although there were near matches. Applying the similarities found that different compounds had different mechanisms. For example, NF_3's reaction with technetium dioxide appeared to follow a phase boundary controlled reaction, while its reaction with uranium dioxide trifluoride at 355°C–365°C followed a 3Ddiffusion controlled reaction mechanism. At higher temperatures, uranium dioxide reaction seems to follow a mechanism closer to a phase-boundary reaction. Reaction kinetics is important for establishing operating parameters for separations process.

Generally, we found that NF_3 is an effective fluorinating and oxidizing agent for selectively producing volatile fluorides at selectable treatment temperatures. Thus, NF_3 is a potentially powerful tool in a fluoride-volatility based used nuclear fuels treatment process.

Isotopic Ratio Fluence Monitors for Canadian Deuterium Uranium (CANDU) and Pebble Bed Modular Reactor (PBMR) Plutonium Production Verification

Mark R. Mitchell, David C. Gerlach, Albert J. Fahey, Christopher J. Gesh, Scott C. Szechenyi

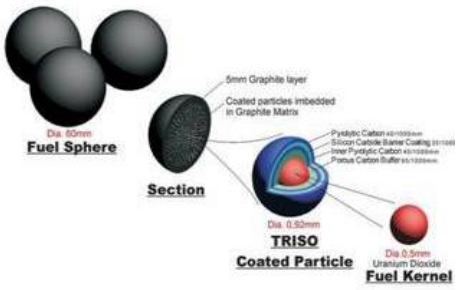
◆ We are developing a concept to create monitoring devices that can be attached to reactor vessels and/or in-core structures, and/or techniques to analyze existing reactor materials, enabling quantification of plutonium produced with sufficient accuracy for safeguards purposes without direct analyses of fuel. The technologies developed will provide a method where adherence to declared reactor operation can be objectively verified. ◆

PNNL has developed and demonstrated techniques for measuring ratios of relative abundance of certain impurity elements for determining the fluence to which ex-reactor materials have been exposed, providing for the ability to calculate the amount of any other isotope produced, including plutonium. While the team has previously demonstrated these measurements using naturally occurring impurity elements, this can be time-consuming and impractical for large numbers of samples. Consequently, PNNL research staff are working to develop IRM techniques for CANDU and PBMR reactors and fuel assemblies that should make such measurements more practical.

Our approach to developing and calibrating these monitoring devices is to conduct irradiation of graphite (for PBMR) and metals (for CANDU) in the Missouri University Research Reactor (MURR) and the Advanced Test Reactor (ATR), followed by analysis at PNNL using a secondary ionization mass spectrometer (SIMS) to establish calibration curves of isotope ratio changes versus fluence. The resulting data and calibration curves should provide a means to quantify plutonium production in both reactor types.

CANDU fuel.

The design of CANDU reactors presents unique nonproliferation and safeguards challenges. With respect to material accountancy, the relatively small physical size of CANDU fuel bundles, their short in-core duty cycle, and the ability of the CANDU reactor to be reloaded while in operation complicate item accounting considerably when compared with light water reactor (LWR). PBMR reactors represent less of a proliferation threat but pose additional and novel safeguards and accounting challenges due to the reactor design. The PBMR uses fuel pebbles rather than traditional pellets housed in fuel rods such as an LWR would use. The sheer number of fuel elements can present an accountability challenge.



Construction of PBMR fuel.

The main accomplishment in FY 2009 was shipping the graphite samples to MURR. For FY 2010, the primary efforts were packaging the graphite samples for irradiation at MURR, irradiation of the samples, receiving shipment of the first samples from MURR to PNNL, and presentations of the work. The first MURR sample was shipped to PNNL in mid-September 2010. This sample was received and the aluminum capsule was opened in a glove box. The capsule was high in activity, which delayed opening and unpackaging. The graphite samples from this first exposure package were then shipped to the SIMS laboratory for analysis.

Original plans were to irradiate metals with graphite at MURR. However, MURR did not have safety analyses on file for these metals, and the cost of obtaining the required analyses would be prohibitive. The team also investigated metals irradiation at the ATR. Meetings with Chalk River personnel revealed two important facts of which we were unaware at the beginning of the project: AECL is not inclined to put flux wires or similar neutron absorbing material in the CANDU reactors, and they routinely remove metal samples from the pressure tubes. These circumstances combine to make analysis of Zircaoly impurities, as we have previously investigated for light water reactors, much more practical than investigating a purpose-built indicator that AECL would be reluctant to use.

Near the end of FY 2011, remaining samples irradiated at MURR were removed for analyses. During FY 2012, analysis of these samples will be completed, with the goal of developing approaches for PBMR reactor accountability. Techniques for analyzing Zircaloy samples currently harvested from CANDU reactors will be refined.

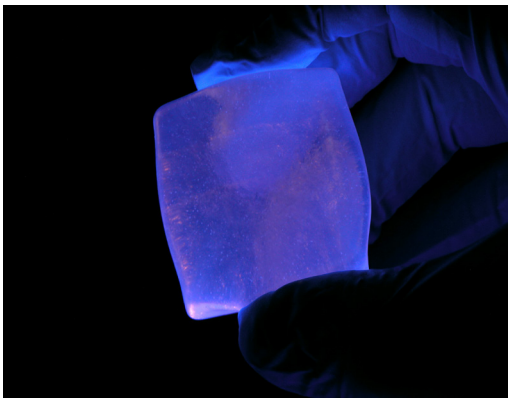
Novel N/gamma Flux Monitoring Materials for Safeguards and Proliferation Detection

Mary Bliss, Ronald J. McConn, Derek A. Haas, Jean A. Stave

◆ This project investigates the fundamental detection properties of bulk thermal neutron-sensitive glass for combined neutron and gamma-ray response for use in compact detector systems. ◆

Recent advances in high-speed electronics make it possible to separate signals from various radiation sources without relying on sample geometry to minimize gamma-ray response so that neutrons can be detected with confidence. The neutron-to-gamma-ray (N/γ) ratio is useful in monitoring and identifying various types of special nuclear material for Arms Control Treaty enforcement. It also has commercial uses in geologic well logging and nuclear energy.

This project will develop, test, evaluate, and potentially deploy uniquely designed materials for neutron and gamma ray monitoring with potential applications in safeguards and proliferation detection. Our work will require fundamental radiation detection material design and development, followed by integration into a prototype detector system with follow-on hardware testing under controlled radiation fields. We will create new instruments for use in locations impossible for ^{3}He detectors, advanced formulations of enriched glass that simultaneously detect thermal neutrons and gamma rays. Energy windowing will also be applied to gain information from gamma ray signals. New signal processing electronics and algorithms will offer the opportunity to use this material in bulk.



A cast piece of PNNL produced neutron sensitive glass (4×4×1.5 cm^3) illuminated with UV light.

Neutron sensitive glass. We developed processes to produce enriched lithium glass of very high optical quality to manufacture into waveguides for large-area neutron detection. The driver was to enhance the neutron signal over gamma rays geometrically. The thin waveguides had minimal gamma ray response when the neutron capture reaction deposited its full energy in a single waveguide. The PNNL waveguides transmit usable signals over lengths of 2 m.

The PNNL-developed manufacturing process produces ^{6}Li glass of exceptional optical properties, but whether bulk pieces could be routinely produced without clouding from phase separation was unknown. Producing a sample of bulk glass was an early goal for this project. A key part of the production effort is to keep cerium in the reduced oxidation state to maximize light emission and minimize absorption.

Signal readout. An XIA PIXIE 500 was procured, along with one pair each of blue and red enhanced Hamamatsu single photon-counting 2.5-cm diameter photomultiplier tubes. An older system was first used to characterize samples on hand. The samples were mounted to the blue-enhanced PMT using optical coupling grease, with the PMT and sample placed inside a light-tight box. Depending on measurement, a ^{252}Cf neutron source was combined with polyethylene moderator to maximize thermal neutron flux and/or 2 in lead shielding to suppress gamma rays. Cadmium foil suppressed thermal neutrons. A ^{137}Cs source was used for gamma ray energy calibration and response.

For pulse-shape processing, each light-generating event is recorded as a function of time, with windows ~10 ns. This is slightly slower but comparable to PMT response. In addition to requiring high-speed electronics for data collection, a large amount of computer memory is needed to store the pulses. One research issue for this project is to define the pulse shape to maximize the differences between gamma rays and neutrons. In addition to pulse shape analysis, Raman spectroscopy was used to explain variations in scintillation light output with glass composition. Raman analysis indicated that the glass samples contain up to three distinct glassy regions, with only one correlating to scintillation brightness.

Physics modeling. MCNP and GEANT models are being developed to determine optimized geometries for bulk enriched lithium glass for neutron interactions. It is currently unknown whether neutrons are slowed inside the glass (increasing detection throughout the bulk) or if this reaction happens only near the surface. These models will be tested using layered structures of enriched and non-enriched glasses.

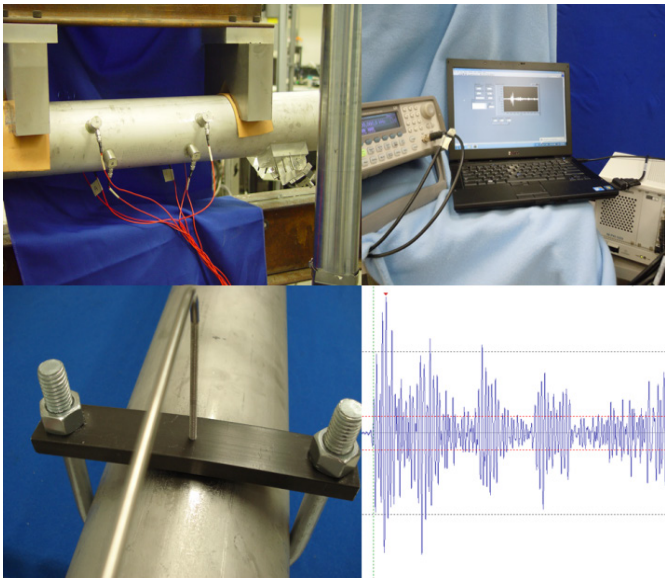
For FY 2012, we will continue to design and develop bulk glass materials as effective neutron detection materials and analyze pulse shapes in response to various forms of radiation for several compositions and forms. With an approach relevant to safeguards, we will attempt to quantify the N/γ selectivity and sensitivity.

On-Line Flaw Detection in Reactor Piping using Acoustic Emission and Guided Wave Ultrasonic Techniques

Ryan M. Meyer, Steven R. Doctor

◆ A shift from periodic local inspections of welds to global continuous monitoring would greatly improve crack detection, especially for the fast-growing flaws. An effective, on-line, continuous monitoring of the pressure vessel and important Class 1 piping systems using acoustic emission and guided wave ultrasound may be able to detect the fast-growing cracks and notify the reactor operators before the cracks cause a leak in reactor components. ◆

A combination of acoustic emission and guided wave ultrasound can be used to monitor a nuclear reactor for cracking in two ways. Acoustic emission sensors can listen passively for characteristic cracking signs during reactor operation. With an array of sensors mounted in strategic locations, one can determine the approximate location of cracking. Guided wave ultrasound uses a series of transducers to project low-frequency ultrasound down the length of a pipe. The ultrasonic wave interacts with discontinuities and returns a series of echoes based on pipe characteristics. The pipe geometry and welds would contribute to a constant ultrasonic signature for the guided-wave system. These waves would be emitted at regular intervals, and specific changes in the reflected and transmitted guided waves would show signs of degradation. While both acoustic emission and guided wave ultrasound have been well developed, they have not yet been used together for continuous online monitoring of nuclear components. Our aim is to experiment with these techniques to allow for continuous on-line monitoring of reactor components for cracking.



Effect of saw cut flaw on guided wave signal.

In FYs 2009 and 2010, a digital 8-channel acoustic emission system was purchased to capture and analyze acoustic emission signals real time. A series of tests using this instrumentation demonstrated that the acoustic emission system could discriminate between noise signals and signals originating from real fatigue flaw growth. Acoustic emission waveguides were also developed and fabricated. The waveguides allow acoustic emission monitoring of components subject to harsh environments by coupling the acoustic emission signal through a long metal rod.

For FY 2011, a software package was purchased to simulate and model guided wave propagation in test specimens. A guided wave ultrasound system has been developed and tested to demonstrate that the guided wave signals are sensitive to large flaws in pipes. A 4-inch diameter stainless steel pipe was fatigue stressed to failure while monitoring the pipe with guided wave ultrasonic transducers and acoustic emission transducers to correlate acoustic emissions and guided wave signals to fatigue crack growth. This experiment was executed, and acoustic emission and guided ultrasonic waved data were archived for further study. This data has been further analyzed using advanced algorithms to cluster signals and help discriminate noise sources from acoustic emission signals resulting from genuine degradation. Waveguides for acoustic emission monitoring have been assessed by a systematic study of the effects of coupling conditions on acoustic emission signal features. Finally, automation of the guided ultrasonic wave instrumentation has also been achieved using commercially available hardware and software.

The results of FY 2009 activities were presented at the American Nuclear Society winter meeting. FYs 2010 and 2011 activities were presented at the 2011 international SPIE/NDE meeting and the 2011 IEEE PHM conference, respectively. These results have also been published in the associated conference proceedings. Our work has also supported three other conference presentations and two conference publications on the use of guided ultrasonic waves and acoustic emission for on-line monitoring in light water reactors and advanced reactors.

Time-Stamped Coincidence-Sampled Gamma-Ray Spectral Data Analysis

Lawrence K. Chilton, Jeremy D. Kephart, Judah I. Friese

◆ We are developing a new capability by combining advanced time-stamped coincidence systems with the analytical tools that will be developed under this research, which will produce the means to identify radioisotopes in nuclear material samples. ◆

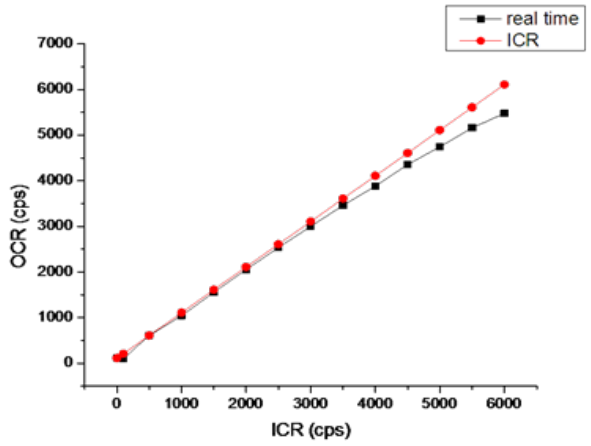
Short-lived isotopes (SLIs) are difficult to detect in part because of how measurements are made. The current practice is to count decays over a period of several days and base assessments on the total number of counts. This assumes the decay source is uniformly constant over the whole period. If an SLI decays during this period, much would occur over only a few hours. Though the total number of decays is small, there could also be a high level of activity during a short period of time. Additionally, SLI materials are present for a relatively short time because their half-lives are so short, plus they are difficult to identify in the environment. However, SLIs are key to several national security problems in nuclear science.

This project is developing analytical tools to address the above issues. Recognizing the challenges with SLIs, PNNL built the Direct Simultaneous Measure (DSM) instrument, which puts a time-stamp on every decay it counts. This project is developing tools to analyze the time-stamped coincidence sampled (TSCS) data produced by the DMS. This will improve the identification of SLIs in radioactive material, which will benefit multiple national security missions, including nuclear nonproliferation, nuclear safety and security, and safeguards.

We have been working on two tasks since the end of FY 2011; both are needed to complete the forward model that will be used to simulate the measurements being made by the DSM and to convert the measurements into SLI assessments (solving the inverse problem). The first task is to model the complex physics involved in isotope decay and the transition from Parent to Daughter isotopes. The key technical achievement is to generate a sequence of decay times for each isotope that is similar to what is happening in real materials. This basic decay sequence generator has been developed and is working. We are extending it to have the flexibility needed for modeling complex materials. We are also doing validation and documentation.

The second task is characterizing dead time and summing in the detector. We developed a single channel simulation code (PIXIsim) that reproduces the dead time as well as the summing corrections for the DSM electronics. This code is used to explore the maximum count rates that a high purity Germanium detector could count based on the time it takes to completely collect the induced charges.

Currently, the PIXIsim code reads in some collection of energy spectra, relative weights, and then rates to sample each. Code samples the spectra produces a list of energy events in linear time, and the code reproduces the digital logic on the list of events. The timing of the energy filters, the pile up rejection, and summing are reproduced for a single HPGe detector. Typical results from this simulation are shown in the figure, where the ICR curve is the ideal response and the real time curve represents the degraded response of a single detector, including dead time. Current work seeks to incorporate the inter-related logic of multiple detectors in the DSM electronics. Experimental verification is crucial to this subtask, so experimental work is also focused on quantifying the dead time of a single DSM detector to a physical model incorporating the digital logic of the electronics.



Ideal versus actual response time as a function of activity (cps).

The most important results to date are that we have a working decay sequence generator which is the technical breakthrough we needed to model and simulate the decay physics in the sample. Additionally, we have a method for modeling and measuring dead time in the detector that enables us to compensate for decays that are missed by the detector due to dead time. We are working on a method to perform this more accurately, which requires a new piece of equipment in FY 2012. Also during the next fiscal year, we will use the validated conceptual model to develop analytical tools to solve the inverse problem of identifying decay chains from measured data. We will design and demonstrate the prototype data analysis tool. Finally, we will track when the inverse problem can and cannot be solved, which will be a function of the complexity of the sample, combinations of similar decay chains, and data noise.

Underground Counting Capability Development and Potential Impacts

Mark D. Engelmann, Paula P. Bachelor

◆ We are working on a multifaceted capability that will capitalize on PNNL expertise to detect ultra-low levels of radioactivity in both gas and solid samples. The developed technologies and analysis protocols will contribute to ground breaking applications, including materials assay, nuclear forensics, age dating, and large-scale physics experiments. ◆

This project was initiated to take advantage of the newly built underground laboratory at PNNL that allows for measurements of ultra-low background (ULB) radiation. The scope involves three tasks where the objective of each is to build one important yet unique aspect of this capability. The three tasks – neutron activation analysis (NAA) and ULB counting, ultra-low radon emanation measurements, and precision gas measurements – all require a highly specialized set of skills and considerations needed when counting very low levels of radioactive materials. The culmination of the tasks will result in a broad-based, world-class suite of capabilities at PNNL related to underground ultra-low level radiation detection.

The research we are conducting is broad with the aim of developing a strong and diverse capability related to underground ULB radiation detection measurements. In general terms, the work is applied research with an aim at building a capability, which will in turn lead to more research. The outcome will leverage PNNL expertise and form the basis for measurement proficiency in various applications, as demonstrated by measurements in a specific subset of applications. Overall, the objective is to use the unique capabilities at PNNL to enable a wide range of ULB measurements in the underground counting facility, leading to worldwide recognition in the scientific community.

After settling on methods and materials as the result of the first-year effort, we spent FY 2010 directing the NAA work towards the challenging isotopic ratio measurement for radioiodine (I-129). I-129 is one of several isotopes so rare relative to their naturally occurring counterparts that ratio measurements are typically possible only by dedicated triple-sector thermal ionization mass spectrometers (TIMS) or accelerator mass spectrometry (AMS). However, TIMS and AMS have limitations that make routine measurement challenging and certainly costly. Because radioiodine is one of the isotopes of most significant concern with respect to nuclear waste management, routine methods of analysis are of great interest. In the case of NAA, the activation product for the major naturally occurring I-127 isotope is relatively short-lived compared with that of the minor radiogenic I-129 isotope, an ideal circumstance for ratio measurements. Therefore, NAA has potential for excellent abundance sensitivity. Favorable neutron-capture cross sections for iodine and a relatively long half-life for the activation product also provide for good absolute sensitivity for the I-129. However, previous NAA methods for radioiodine required post-irradiation separation. ULB counting techniques may obviate the need for post irradiation sample handling and still provide competitive sensitivity of the iodine isotopic determination, thereby providing by far the best overall measurement technique for the needs of the nuclear industry.

We performed three rounds of iodine sample irradiations with four quantities of iodine that spanned several orders of magnitude. The iodine isotopes were easily detected in the first irradiation (highest sample). For the second irradiation, we chose to analyze a sample that represented a significant challenge, and the iodine activation products were not resolvable from the interfering activation products of the quartz and process impurities in the sample ampoule. For the third, we chose two intermediate quantities. While the iodine was detectable, the sensitivity of the method is severely limited by the presence of impurities in the quartz or other residual matrix components.

For our ultra-low radon emanations task, simulations of an ULB copper gas proportional counter determined an 83% volumetric efficiency for the system. Because the radon (Rn) alpha energies are well above the counter's background and low-energy threshold, a Rn alpha counting efficiency was also expected to be ~83%. Leveraging prior work on DOE funded projects and updating concepts found in research literature, the Rn emanation bench was designed and built during the first year of the project. Baselines were established for above and below ground counting with the ULB copper proportional counters of PNNL design using pure P10 gas. A background sample from the gas system was counted on a ULB proportional counter above ground with no counts in the region of interest, which indicates the Rn assay process would not benefit from being placed underground. Preliminary test results suggest the detection of Rn based on measurements made from a calibration sample of a single Zeolite pellet with an emanation rate of 200 radon atoms. A 24 hr energy spectrum detected 245 counts in the Rn energy window. During multi-day runs, the number of counts decreased with time; an exponential fit gives half-life of 3.4 days, which is in agreement with the Rn half-life of 3.8 days within experimental error. Also observed was a "wall" in the energy spectrum at 5.3 MeV which compares with primary Rn α-decay of 5.5 MeV. Currently, the Rn emanation bench is being modified by installing a new sample chamber, which

can accommodate the non-destructive evaluation of CoGeNT's large insulator samples.

The objective of our precision gas counting task was to develop a capability at PNNL to determine the activity concentration of gas samples without the need of calibration reference-gases. The method proposed is referred to as Length-Compensated Internal-Proportional-Counting (LC-IPC). PNNL wished to develop this unique measurement technique and apply it to analysis of low activity samples, consistent with operations in PNNL's underground counting facility. In FY 2010, a measurement test apparatus was designed and constructed, and testing was initiated in the second year of the project. One objective of this project not achieved was the fabrication of custom PNNL IPCs built from ultra-low background materials; it was decided early on in the project to focus resources on maturing the measurement technique with less costly commercial detectors and then gravitate towards ULB counters once the method had been tested.

For FY 2011, several measurement campaigns were conducted on this procured gas sample, and the complete LC-IPC analysis method was applied to the data with enlightening results. On average, the analysis resulted in activity concentrations of the gas sample that were quite appropriate; however there were real inconsistencies between the detectors used in the measurements. Using three detectors allows for three differences to be determined and used in the analysis. If four detectors were used, it would allow for six differences. In addition to having double the number of results to use in the analysis, four detectors would allow for consistency checks, while using only three detectors eliminates this feature. The final result of this effort was that PNNL developed the working knowledge to conduct these measurements; however, additional effort is required to resolve the detector inconsistency issue.

Physics

Dark Matter Science and Detector Development

John L. Orrell, Erin S. Fuller, James E. Fast, Todd W. Hossbach, Marek S. Kos, Richard T. Kouzes, Cory T. Overman, Brent A. Vandevender

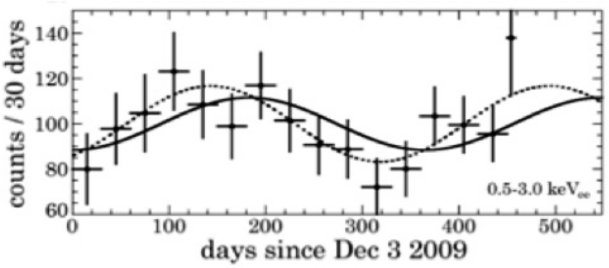
◆ We aim to develop the next generation of dark matter detectors that contain low-capacitance mount, noise reduction, and ultra-low background technique characteristics. ◆

Unambiguous direct detection of cosmological dark matter particles is, perhaps, the single most pressing particle astrophysics measurement sought by cosmologists and theoretical particle physicists alike. Dark matter is well known by its gravitational effects observed throughout the universe, despite being entirely invisible to our telescopes measuring the electromagnetic spectrum from radio frequencies, through the visible spectrum, and up to gamma rays. Gravitational effects appear in deviations from uniform intensity of the cosmic microwave background radiation, galactic clustering, gravitational lensing, and the rotation of galaxies. The leading theoretical candidate for these effects is the presence of a weakly interacting massive particle (WIMP) whose gravitational influence is ubiquitous but otherwise does not participate in the electromagnetic or strong interactions of the standard model of particle physics.

Public and scientific interest in dark matter stems from the glaring realization that scientists and researchers know and understand only a small fraction of the matter that composes the universe. From the last century of physical research, science can claim familiarity with only ~17% of the universe's matter composed of heavy elements, neutrinos, stars, and free hydrogen and helium produced by the Big Bang. The remaining 83% is some yet to be measured material – the dark matter – that we can infer must exist from its gravitational imprints throughout the universe but is otherwise unknown to science.

This project analyzed data from the CoGeNT Dark Matter Experiment located at the Soudan Underground Laboratory in a search for a predicted annual modulation of the radiation detector's event rate induced by dark matter interactions that vary over the year. We are also developing a next generation approach, the C4 Dark Matter Experiment, intended to test in detail the previous year's unexpected results from CoGeNT showing an excess of events at low energy that is compatible with a low-mass (<10 GeV/c^2) dark matter particle origin.

In the previous year, CoGeNT experiment results pointed to a region of dark matter parameter-space (particle mass, m_x, and interaction cross section, σ_{SI}) consistent with a low-mass (<10 GeV/c^2) dark matter particle. This was entirely unexpected and surprising because it roughly matched the experimental results from DAMA, a long-running experiment that for years claimed to see an annual modulation in their detectors' event rate consistent with a dark matter interaction rate changing as the earth orbits the sun. This annual modulation event rate in dark matter signal rate is theoretically expected due to earth's changing velocity relative to the theorized halo of dark matter present in the galaxy. As earth is moving with the sun's orbit around the Milky Way in June, dark matter-induced nuclear recoils have a boosted energy. As earth moves in the opposite direction in December, nuclear recoils have a suppressed energy spectrum.



Temporal variation of the low-energy event rate of CoGeNT (points and free sine-wave fit, dashed line). A dark-matter signal is expected to be at minimum in December and modulate annually (solid line).

In the last year of project work, analysis of 15 months of data collected from the CoGeNT detector was analyzed for the presence of any modulation of the event rate of the excess of events at low energy. Although not statically significant, the data does hint that a modulation – like that anticipated from a dark matter source – could be present. We have worked on developing an experimental design to test the CoGeNT results. We have also successfully prepared a full shield design for the expanded C4 Dark Matter Experiment that is intended to confirm or refute the CoGeNT finding. The C4 Dark Matter Experiment will have 10 times the target mass giving the experiment greater sensitivity to a low-mass dark matter signal, should it exist. The experiment will employ multiple detectors allowing cross-comparison for consistency and ruling-out non-dark matter-related systematic effects in the experiment. The greater sensitivity will allow for a detailed examination of the low-energy region of record events as well as dramatically improving the ability to search for the annual modulation effect.

Other dark matter experiments are ongoing at other laboratories around the world. Independent and convincing evidence from several experiments is required for the community to finally claim discovery of dark matter. The C4 Dark Matter Experiment is one particularly capable instrument intended to test the low-mass WIMP hypothesis and clarify the preliminary results from the CoGeNT Dark Matter Experiment.

Low Level Argon-42 Measurement Analysis (LLAMA)

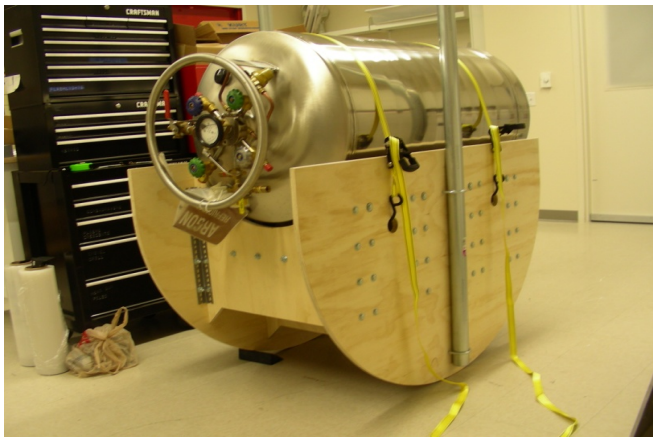
Judah I. Friese, Rosara F. Payne, Jeremy D. Kephart,
Brian D. Glasgow, Debra S. Barnett, Erin C. Finn

◆ The amount of ^{42}Ar in the atmosphere is not well known but very important to many large scale ultra low-level science experiments. We will attempt to measure the amount of ^{42}Ar in the atmosphere to enable a much greater these large scientific challenges. ◆

A handful of published scientific articles have theorized the physical process involved in ^{42}Ar production in the atmosphere and what concentration currently exists. Only a few papers have attempted to measure the atmospheric concentration of ^{42}Ar. Current technology has only been able to place upper limits because of the ultra low concentrations of ^{42}Ar in the atmosphere. By attempting to measure the atmospheric concentration of ^{42}Ar, we must push the limits of ultra-low atmospheric measurements.

In this project, we have developed a method to extract samples of ultra-low concentration ionic atoms from a large volume of liquefied gas. The direct detection of the ^{42}Ar is not reasonable or feasible (long half-life, no associated gammas). The daughter substance, ^{42}K, has a shorter half-life (12.36 hr vs. 33 yr) and emits a 1525 keV gamma for ~18% of the decays. We needed to develop a method to extract and concentrate the ^{42}K from 280 L of liquid argon. The ^{42}K was allowed to reach equilibrium and plate out on the inner surface of the tank. The liquid argon was removed as quickly as possible, leaving the ^{42}K on the inner surface. Many trials were needed to optimize the time of sampling processing (tank heat time, rinse and evaporation time), which is directly linked to the sensitivity of the measurement. We have designed and built the rinse mechanism for a 280 L dewar with nitric acid rinse chemistry. This mechanism allowed for rinsing of all surfaces of the tank while minimizing the volume of acid needed, thereby decreasing the sample processing time. The inner surface was rinsed with a low concentration acid to remove the K ions ionically from the inner surface. The acid rinse volume was reduced through evaporation into a sample suitable for gamma spectrometry. The samples generated through this process were counted in the underground counting facility on high efficiency low background detectors.

Besides the development and execution of the method to extract extremely low concentrations of a rare isotope out of a large volume of liquefied gas, this project also made several other significant advances. We have developed and used a chemical tracer process to monitor quality controls in the entire experimental process. We helped to develop a neutron activation tracer gas handling system with the University of Texas at Austin. We also established a relationship with the GERDA experiment and Max Plank Institute for Physics, in Germany. This work developed an in-depth understanding of ultra-low background detection limits.



The rinse mechanism with a 440 lb, 280 L liquid argon dewar. The low volume, low concentration nitric acid is placed inside the dewar, and the internal walls are rinsed as the dewar is re-orientated.

After chemical processing and gamma spectrometry, the samples collected to date show that no ^{42}Ar was detected. This places the concentration of ^{42}Ar below the first run detection limits. We can assume one of two important things from this null measurement: either the chemistry was not as we understood it to be or given some collection efficiency, the ^{42}K level is much lower than expected. The amount of ^{40}K in the sample implies that the collection efficiency is high. Further research is needed to better understand the collection efficiency at each step of the experiment as well as the true ^{42}Ar atmospheric concentration.

Any small amount of radioactivity can have significant implications for many large-scale physics experiments that are searching for unique signals such as those from double beta decay and the hunt for dark matter. These ultra-low background measurements have a need to understand all possible sources of background present in the system. Argon-42 has been known to be a small source of background due to its presence in the atmosphere and in liquid argon. This work combined ultra-sensitive separations with ultra-low background detection techniques to experimentally determine a quantitative upper limit of ^{42}Ar in the atmosphere with higher confidence than has been set in the past. This work will have significant impacts for understanding and interpretation of the large-scale physics experiments being operated around the world.

Photon Signatures for Enhanced Bulk and Residue Explosives Detection

Timothy A. White, Bruce E. Bernacki, Erin A. Miller, Mark C. Phillips

◆ This project investigates signatures for both bulk explosives and explosives residue, using image-based active-interrogation techniques. These non-contact evaluation methods in both the x-ray and infrared regions of the electromagnetic spectrum offer enhancements in material-discrimination capabilities over conventional interrogation techniques. Success in these investigations will impact standoff and portal-based explosives-detection techniques. ◆

Recent developments based on x-ray refraction, in addition to absorption using a conventional x-ray source, result in three physically distinct contrast mechanisms for bulk detection of explosives: absorption, phase, and scatter. Exploitation of these modes for improved explosives detection has not been fully explored. A system will be constructed to perform computed tomography measurements in all three modes to perform this investigation. The resulting data will be analyzed to extract materials signatures; this method for material discrimination will be quantitatively compared with other x-ray material discrimination methods such as dual- or multiple-energy analysis.

Enhanced detection of explosive residue will exploit infrared spectroscopy using a broadly tunable external cavity quantum cascade laser (ECQCL) to perform standoff hyperspectral imaging. Explosives can be identified and distinguished from background based on their characteristic infrared spectra, where broadly tunable illumination is essential to acquire sufficient spectral data for positive identification. Active ECQCL illumination will enable longer standoff distances and targeted illumination, while producing an image hypercube enabling the use of mature statistical methods developed by the passive hyperspectral-imaging community. Together, these complimentary detection capabilities could form the basis for next-generation multimodal security screening systems, such as for baggage screening.

Two main accomplishments from the x-ray/bulk-detection task were the investigation of the scatter signal from phase contrast x-ray imaging and development of a computed tomography capability for all three contrast modes. The scatter signal can be related to the features in the object that are below the spatial resolution of the imaging system. Some explosives contain texture or inclusions ranging in size from microns to hundreds of microns and the scatter information may allow exploitation of those features for discrimination of explosive from benign material. A study of glass spheres of known size using a three-grating interferometer, demonstrated sensitivity to textures specifically in this size range as well as an ability to distinguish samples on the basis of feature size. This work was presented at the annual IEEE Nuclear Science Symposium. Three-grating system performance was improved through small changes to gratings manufacturing and materials, leading to a doubling of signal-to-noise ratio. A new experiment – a simple single-grating version of the phase-contrast technique – was also tested. This system demonstrated the ability to distinguish nanoparticles (8, 30, and 1000 nm iron oxide) that are at least three orders of magnitude smaller than the imaging resolution of the radiography system. Also, it is possible to tune the system to be sensitive to different sample characteristics. Finally, acquisition and processing software were developed, which allowed a collection of computed tomography data and independent reconstruction of all three contrast modes into three-dimensional images.

The residue detection task concentrated on three topics: measurements of diffuse infrared laser scattering from explosives on realistic surfaces; development of an understanding of scattering spectroscopy from particles on surfaces; and additional analysis of hyperspectral microscopy for trace detection. The literature has little information on scattering from non-ideal surfaces, and understanding competing absorption, transmission, and reflection from the residue and substrate will impact detectability. To further this understanding, experiments exploring a multidimensional parameter space were developed. The parameters included varying illumination and detection angle, standoff distance, sample concentration and morphology, and substrate. These data enabled an understanding of observed spectra and allowed development of models to describe observations. The results were presented at two conferences and generated invitations for talks at four conferences for FY 2012. Two peer-reviewed publications are also in preparation.

Our investigations lay the groundwork for developing new x-ray systems for secondary screening in a security setting and enhanced material discrimination and detection for other x-ray interrogation measurements such as non-destructive evaluation or medical imaging. Standoff hyperspectral infrared measurement and analysis developed under this project could be used in standoff portal monitoring applications to screen cargo, vehicles, or people (lasers operate at eye-safe levels) for the presence of explosive residue without surface contact or a cooperative target. A portable handheld instrument is feasible for tactical deployment or use by first responders. Work in all areas continues to enhance PNNL's capabilities in explosives detection and active interrogation.

Appendix A

Fiscal Year 2011 Refereed Publications

Appendix A

Fiscal Year 2011 Refereed Publications

During FY 2011, PNNL's LDRD Program resulted in 127 refereed publications. These journals articles, book chapters, and select conference papers are listed below in alphabetical order by the author's last name.

Aalseth CE, PS Barbeau, J Colaresi, JI Collar, J Diaz Leon, JE Fast, N Fields, TW Hossbach, ME Keillor, JD Kephart, A Knecht, MG Marino, HS Miley, ML Miller, JL Orrell, DC Radford, JF Wilkerson, and KM Yocum. 2011. "Search for an Annual Modulation in a *p*-Type Point Contact Germanium Dark Matter Detector." *Physical Review Letters* 107(14), Art 141301.

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Zhao Y, Y Yang, CA Mims, CHF Peden, J Li, and D Mei. 2011. "Insight into Methanol Synthesis from CO_2 Hydrogenation on Cu(111): Complex Reaction Network and the Effects of H_2O." *Journal of Catalysis* 281(2):199-211.

Zhong L, JE Szecsody, M Oostrom, MJ Truex, X Shen, and X Li. 2011. "Enhanced Remedial Amendment Delivery to Subsurface Using Shear Thinning Fluid and Aqueous Foam." *Journal of Hazardous Materials* 191(1-3):249-257.

Appendix B

Fiscal Year 2011 Non-Refereed Publications

Appendix B

Fiscal Year 2011 Non-Refereed Publications

In this appendix, 250 non-refereed publications or presentations resulting from PNNL's LDRD Program during FY 2011 are arranged in alphabetical order by the first author's last name.

2011. PNNL-20306 [Limited Distribution]

Acharya DP, X Lin, BD Kay, Z Dohnalek, and Z Zhang. 2011. "Direct Visualization of Adsorption and Dissociation of Propane-1, 3-diol Molecules on TiO_2(110)." Presented by Danda P. Acharya at Symposium 2011 AVS Pacific Northwest Chapter, Wilsonville, OR, September 15, 2011.

Adami S, XY Hu, NA Adams, EM Ryan, and AM Tartakovsky. 2011. "A Fully Coupled 3D Transport Model in SPH for Multi-Species Reaction-Diffusion Systems." Presented by Alexandre M. Tartakovsky at 6th SPHERIC International Workshop, Hamburg, DEU, June 9, 2011.

Adami S, XY Hu, NA Adams, EM Ryan, and AM Tartakovsky. 2011. "A Fully Coupled 3D Transport Model in SPH for Multi-Species Reaction-Diffusion Systems." In *Proceedings of the 6th SPHERIC International Workshop*, Hamburg, DEU, pp. 187-193. SPH European Research Interest Community, Manchester, UK.

Anderson KK, Z Huang, Y Li, P Du, R Diao, and B Lee. 2011. "Sensitivity Analysis of the Kalman Filter and Its Applications in Power Systems." Presented by Pengwei Du at IEEE PES Conference on Innovative Smart Grid Technologies (ISGT 2011), Anaheim, CA, January 18, 2011.

Anheier Jr NC. 2010. "Integrated Air Collection and Measurement System for Enrichment Plant Safeguards." Presented by Norman Anheier (invited speaker) at IAEA Symposium on International Safeguards: Preparing for Future Verification Challenges, Vienna, AUT, November 1, 2010.

Anheier Jr NC and BA Bushaw. 2010. "Unattended Environmental Sampling and Laser-Based Enrichment Assay for Detection of Undeclared HEU Production in Enrichment Plants." In *Proceedings of the Pacific Northwest International Conference on Global Nuclear Security - The Decade Ahead*, April 11-16, 2010, Portland, OR. INMM, Deerfield, IL.

Anheier Jr NC, JT Munley, and ML Alexander. 2011. "Design of an Unattended Environmental Aerosol Sampling and Analysis System for Gaseous Centrifuge Enrichment Plants." In *Proceedings of the INMM 52nd Annual Meeting*, Palm Desert, CA, July 17-21, 2011. INMM, Deerfield, IL.

Anheier Jr NC, JT Munley, and ML Alexander. 2011. "A New Unattended Environmental Sampling and Analysis Paradigm for Gaseous Centrifuge Enrichment Plants." Presented by Norm C. Anheier at INMM 52nd Annual Meeting, Palm Desert, CA, July 21, 2011.

Bacon DH and EM Murphy. 2010. "Managing Chemistry Underground: Is Co-Sequestration an Option in Selected Formations?" Presented by Diana H. Bacon at International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, NLD, September 22, 2010.

Baer DR, NJ Hess, DW Hoyt, AS Lea, and CM Wang. 2010. "Developing Unique Research Tools to Study Carbon Sequestration and Energy Storage." Presented by Don Baer at 219th Electrochemical Society (ECS) Meeting, Montreal, CAN, May 4, 2011.

Baer DR, NJ Hess, DW Hoyt, AS Lea, and CM Wang. 2010. "Developing Unique Research Tools to Study Carbon Sequestration and Energy Storage." In *219th Electrochemical Society (ECS) Meeting Abstracts*, Montreal, CAN, May 1-6, 2011. ECS, Pennington, NJ.

Baer DR, NJ Hess, DW Hoyt, AS Lea, and CM Wang. 2011. "Unique In-Situ Tools to Study Carbon Sequestration and Energy Storage." Presented by Don Baer (invited speaker) at European Conference on Applications of Surface and Interface Analysis 2011, Cardiff, UK, September 5, 2011.

Bailey VL, SJ Fansler, and LA McCue. 2011. "Linking Genomic Structure to Function in Soil Aggregates." Presented by Vanessa Bailey at ISMOM 2011, Montpellier, FRA, June 28, 2011.

Bailey VL, SJ Fansler, LA McCue, A Konopka, H Bolton, Jr, and MJ Wilkins. 2010. "Microbial Communities Research at PNNL." Presented by Vanessa Bailey (invited speaker) at WSU Department of Crop and Soil Sciences Seminar Series, Pullman, WA, October 25, 2010.

Bandara UC, AM Tartakovsky, and BJ Palmer. 2011. "Pore-Scale Investigation of CO_2 Trapping Mechanisms in Geological Formations." Presented by Uditha Bandara at 10th Annual Carbon Capture and Sequestration Conference, Pittsburgh, PA, May 3, 2011.

Barker EI, D Li, X Sun, and MA Khaleel. 2011. "3D Microstructure Generation and Simulation for the Prediction of Mg Ductility." Presented by Erin I Barker at ICME, Seven Springs, PA, July 13, 2011.

Beliaev AS. 2010. "Synthetic Bioengineering Approaches for High-Density Fuel Production in Cyanobacteria." Presented by Alex Beliaev at Pacific Rim Summit on Industrial Biotechnology and Bioenergy, Honolulu, HI, December 13, 2010.

Beliaev AS. 2011. "Synthetic Bioengineering and Systems Biology of Cyanobacteria for Bioenergy Applications." Presented by Alex Beliaev (invited speaker) at 2011 World Congress on Industrial Biotechnology and Bioprocessing, Toronto, ON, Canada, May 9, 2011.

Beliaev AS. 2011. "Systems Biology and Bioengineering of Cyanobacteria for Bioenergy Applications." Presented by Alex Beliaev (invited speaker) at MCCMB 11, Moscow, Russian Federation, July 22, 2011.

Bliss M, DA Haas, JA Stave, JV Ryan, and JW Hayes. 2011. "Scintillating Glasses for Specialized Applications." Presented by Mary Bliss (invited speaker) at SCINT 2011, Giessen, GER, September 14, 2011.

Bond LJ, P Ramuhalli, N Lybeck, and M Tawfik. 2011. "Prognostics and Life Beyond 60 for Nuclear Power Plants." Presented by Pradeep Ramuhalli at PHM2011: 2011 IEEE International Conference on Prognostics Health Management, Denver, CO, June 22, 2011.

Bond LJ, RM Meyer, and P Ramuhalli. 2011. "Advanced NDE, Diagnostics and Prognostics Research at PNNL." Presented by Ryan Meyer at 2nd Annual U.S. Department of Energy Nuclear Energy Programs Materials Science and Engineering Materials Cross-Cut Works, Berkeley, CA, June 21, 2011.

Bond LJ, RM Meyer, and P Ramuhalli. 2011. "Online Monitoring to Enable Improved Diagnostics, Prognostics and Maintenance." Presented by Leonard J Bond (invited speaker) at ICI 2011, Daejeon, Republic of Korea, August 23, 2011.

Bylaska EJ, JQ Weare, SB Baden, and JH Weare. 2011. "Improving the Accuracy and Time Scales of ab initio molecular dynamics simulations: Exact Exchange, MP2, and Parallel in Time Algorithms." Presented by Eric Bylaska (invited speaker) at American Chemical Society Fall Meeting 2011, Denver, CO, August 29, 2011.

Camaioni DM, AJ Karkamkar, K Parab, and T Autrey. 2011. "Activation of H_2 by Non-Metals for Energy Storage in Chemical Bonds." Presented by Bojana Ginovska at the 242nd American Chemical Society (ACS) National Meeting, Denver, CO, August 31, 2011.

Carson JP, T Nguyen, DE Harrington, YL Hai, U Kurkure, MA Enlow, L Kindle, I Kakadiaris, and T Ju. 2010. "New Tools for Multiscale Cell-to-Organ Modeling using Deformable 3D Atlases." Presented by James Carson at BMES 2010, Austin, TX, October 8, 2010.

Carson JP. 2010. "Registration of High Resolution Serial Histology Data." Presented by James Carson (invited speaker) at Cold Spring Harbor Laboratory Online Conference, November 5, 2010.

Casella AJ, TG Levitskaia, and JM Peterson. 2010. "CO_2 Separation and Capture by Chitosan Materials." Presented by Amanda Casella, Electric Power, Rosemont, IL, May 10, 2010.

Casella AJ, TG Levitskaia, JM Peterson, TA Robinson, CE Rutherford, OS Muzaffery, AM Lines, M Nilsson, and SA Bryan. 2011. "On-Line Monitoring Techniques for Spent Fuel Reprocessing." Presented by Amanda Casella at International High-Level Radioactive Waste Management Conference, Albuquerque, NM, April 11, 2011.

Casella AM, RD Scheele, and BK McNamara. 2011. "Gathering Kinetic Data from Fluorination of Actinides with NF_3." Presented by Andy Casella at 35th Annual Actinide Separations Conference, Charlotte, NC, May 23, 2011.

Chavarría-Miranda D, JA Daily, S Krishnamoorthy, MK Krishnan, BJ Palmer, and A Vishnu. 2010. "Global Arrays Roadmap & Future Developments." Presented by Daniel Chavarría-Miranda (invited speaker) at ACM/IEEE International Conference for High Performance Computing, Networking, Storage and Analysis, New Orleans, LA, November 18, 2010.

Chavarría-Miranda D, JA Daily, S Krishnamoorthy, MK Krishnan, BJ Palmer, and A Vishnu. 2011. "Global Arrays: Into the Future." Presented by Daniel Chavarría-Miranda (invited speaker) at Future Approaches to Data Centric Programming for Exascale, Anchorage, AK, May 20, 2011.

Chen Y and Z Huang. 2010. "An Advanced Framework for Enabling Electricity Infrastructure Real-Time Decision Support." Presented by Yousu Chen at Second International Conference on Computational Sustainability, Cambridge, MA, June 30, 2010.

Chen Y and Z Huang. 2011. "Graphical Contingency Analysis Tool." Presented by Yousu Chen (invited speaker) at 2011 EMS Users Conference, Philadelphia, PA, September 19, 2011.

Chen Y, Z Huang, and N Zhou. 2011. "An Advanced Framework for Improving Situational Awareness in Electric Power Grid Operation." Presented by Yousu Chen (invited speaker) at the 18th IFAC World Congress, Milan, ITA, August 31, 2011.

Clowers BH. 2011. "Signal to Noise Ratio Comparison of Direct Charge Integration and Current Amplification." Presented by Brian Clowers at International Society for Ion Mobility Spectrometry 2011, Scotland, UK, July 28, 2011

Du P, Z Huang, Y Sun, R Diao, K Kalsi, KK Anderson, Y Li, and B Lee. 2011. "Distributed Dynamic State Estimation with Extended Kalman Filter." In *Proceedings of 43rd North American Power Symposium*.

Edgar TW, DO Manz, and PA Boyd. 2011. "Water Substation Demonstration." Presented by David O. Manz at DETER/DEFT Group Meeting, Los Angeles, CA, January 25, 2011

Engel DW, ML Gregory, EB Bell, and LR McGrath. 2011. "Identifying On-Line Groups Based on Content and Collective Behavioral Patterns." Presented by Dave Engel (invited speaker) at IADIS International Conference, July 18, 2011.

Enke C, SJ Ray, AW Graham, E Dennis, GM Hieftje, DW Koppenaal, CJ Barinaga, and AJ Carado. 2011. "Distance-of-Flight Mass Analysis A New Tool for Atomic Spectrometry." Presented by Dave Koppenaal (invited speaker) at Pittcon Conference 2011, Atlanta, GA, March 14, 2011.

Enke C, SJ Ray, AW Graham, GM Hieftje, DW Koppenaal, CJ Barinaga, and AJ Carado. 2010. "Elemental Analysis by Distance-of-Flight MS and Array Detection." Presented by Chris Enke at ASMS 58th Conference on Mass Spectrometry and Allied Topics, Salt Lake City, UT, May 25, 2010.

Ewing RG, MJ Waltman, and DA Atkinson. 2011. "Equilibrium Vapor Pressures of Explosive Compounds at Ambient Temperatures." Presented by Robert Ewing (invited speaker) at Trace Explosives Detection Workshop, Portland, OR, April 11, 2011.

Fan J, X Liu, GR Kulkarni, and M Ovchinnikov. 2011. "Toward Improving Ice Nucleation Parameterization based on Classical Nucleation Theory." Presented by Jiwen Fan at IUGG XXV General Assembly Earth on the Edge: Science for a Sustainable Planet, Melbourne, AUS, June 28, 2011.

Fast JD and PJ Rasch. 2011. "Using ISDAC Data as a Testbed for Evaluating the Performance of CAM5 Physics Treatments in the Arctic." Presented by Jerome Fast and Phil Rasch (invited speakers) at ISDAC: Observation to Modeling Breakout Session, ASR Science Team Meeting, San Antonio, TX, March 29, 2011.

Fast JD, RC Easter, Jr, X Liu, SJ Ghan, and PJ Rasch. 2011. "A Computationally Efficient Aerosol Model from the CAM5 Climate Model Ported into WRF." Presented by Jerome D. Fast at 12th WRF User's Workshop, Boulder, CO, June 22, 2011.

Fast JD, WI Gustafson, Jr, B Singh, RC Easter, Jr, and PJ Rasch. 2010. "Using Testbeds to Evaluate Aerosol Simulations over Multiple Spatial Scales." Presented by Jerome Fast at 2010 American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 15, 2010.

Fast JD, WI Gustafson, Jr, RC Easter, Jr, B Singh, and PJ Rasch. 2011. "A Framework for Evaluating the CAM5 Physics Suite at High Spatial Resolution in WRF." Presented by Jerome D. Fast at 12th WRF User's Workshop, Boulder, CO, June 23, 2011.

Ferryman TA, FK Tuffner, N Zhou, and G Lin. 2011. "Predictability of Real Power on the Grid Using PMU Data." Presented by Guang Lin (invited speaker) at 2011 IEEE PES Power Systems Conference and Exhibition (PSCE), Phoenix, AZ, March 21, 2011.

Follum JD, N Zhou, and JW Pierre. 2011. "Evaluation of Mode Estimation Accuracy for Small-Signal Stability Analysis." Presented by Jim Follum at North American Power Symposium 2011, Boston, MA, August 6, 2011.

Garza JM and D Chavarría-Miranda. 2010. "Extending the Global Arrays Programming Model to Hybrid Architectures." Presented by Daniel Chavarría (invited speaker) at Global Arrays Technical Meeting, Seattle, WA, May 6, 2010.

Garza JM and D Chavarría-Miranda. 2010. "Global Arrays Roadmap." Presented by Daniel Chavarría (invited speaker) at Global Arrays Technical Meeting, Seattle, WA, May 6, 2010.

Gibson TD and EG Stephan. 2008. "Application of Provenance for Automated and Research Driven Workflows." Presented by Tara Gibson at Second International Provenance and Annotation Workshop, Salt Lake City, UT, June 17, 2008.

Gibson TD and EG Stephan. 2009. "Provenance: From Arts to Systems Science." Presented by Tara Gibson at SLAC Presentation, Palo Alto, CA, September 11, 2009.

Gibson TD, KL Schuchardt, and EG Stephan. 2009. "Application of Named Graphs Towards Custom Provenance Views." Presented by Tara Gibson at 1st Workshop on the Theory and Practice of Provenance (TaPP '09), San Francisco, CA, February 23, 2009.

Gibson TD, KL Schuchardt, EG Stephan, and PR Paulson. 2007. "Semantic Data Grid (SDG) 2nd Provenance Challenge." Presented by Tara Gibson at High-Performance Distributed Computing - Second Provenance Challenge workshop, Monterey, CA on June 26, 2007.

Gorton I. 2011. "An Architectural Blueprint for Service-Based Science in the Cloud." Presented by Ian Gorton (invited speaker) at COMPARCH 2011, Boulder, CO, June 22, 2011.

Gorton I, Y Liu, AV Kulkarni, and AS Wynne. 2011. "Towards Composing Data Aware Systems Biology Workflows on Cloud Platforms." Presented by Jenny Liu (invited speaker) at IEEE 2011 Services Congress – Fifth International Workshop on Scientific Workflows (SWF 2011), Washington, D.C., July 5, 2011.

Gosney A, CS Oehmen, and I Gorton. 2011. "An Adaptive Middleware Framework for Optimal Scheduling On Large Scale Compute Clusters." Presented by Arzu Gosney (invited speaker) at 8th International Conference on Information Technology: New Generations, Las Vegas, NV, April 12, 2011.

Graff GL, J Liu, J Zhang, Z Yang, JP Lemmon, JZ Hu, and KM Rosso. 2011. "Energy Storage for Transportation and Grid Applications." Presented by Gordon Graff (invited speaker) at POSCO/RIST, January 25, 2011.

Graham AW, SJ Ray, CJ Barinaga, DW Koppenaal, C Enke, and GM Hieftje. 2010. "Distance of Flight Mass Spectrometry: A New Instrumental Concept for Elemental Mass Spectrometry." Presented by David W. Koppenaal (invited speaker) at FACSS 2010 Conference, Raleigh, NC, October 19, 2010.

Gregory ML, DW Engel, EB Bell, AW Piatt, ST Dowson, and AJ Cowell. 2011. "Automatically Identifying Groups Based on Content and Collective Behavioral Patterns of Group Members." In *Proceedings of the Fifth International AAAI Conference on Weblogs and Social Media*, pp. 498-501.

Greitzer FL. 2011. "A Hierarchical Reasoning Framework for Threat Analysis and Anticipation." Presented by Frank L. Greitzer (invited speaker) at Computational Cybersecurity in Compromised Environments (C3E), Keystone, CO, September 26, 2011.

Greitzer FL. 2011. "Insider Threat Behavioral Analysis." Presented by Frank L. Greitzer (invited speaker) at DOE Cyber Security Workshop, Kansas City, MO, May 3, 2011.

Greitzer FL. 2011. "Insider Threat: Guest Lecture." Presented by Frank L. Greitzer (invited speaker) at University of Hawaii Online Course ICS426, University of Hawaii, September 16, 2011.

Haack JN and GA Fink. 2011. "Information Requirements of Emergence." Presented by Jereme Haack at Computational Cybersecurity in Compromised Environments, Keystone, CO, September 26, 2011.

Hazelton SG, M Liezers, BE Naes, LM Arrigo, and DC Duckworth. 2011. "Electrochemically-Modulated Separations for Material Accountability Measurements." In *Proceedings of the INMM 52nd Annual Meeting*, Palm Desert, CA, July 17-21, 2011. INMM, Deerfield, IL.

Hazelton SG, M Liezers, BE Naes, LM Arrigo, DC Duckworth, and JM Schwantes. 2011. "Electrochemically-Modulated Separations for Material Accountability Measurements." Presented by Sandra Hazelton at the INMM 52nd Annual Meeting, Palm Desert, CA, July 20, 2011.

Heath BS, PJ Roach, J Laskin, MJ Marshall, DF Smith, L Pasa-Tolic, Z Zhu, JD Watrous, and PC Dorrestein. 2011. "Identification of Mechanisms of Extracellular Respiration by *Shewanella oneidensis* MR-1 Using Imaging Mass Spectrometry." Presented by Brandi S. Heath, ASMS 59th Conference on Mass Spectrometry and Allied Topics, Denver, CO, June 7, 2011.

Heldebrant DJ. 2011. "Binding Organic Liquids for Natural Gas Purifications." Presented by David Heldebrant at the American Chemical Society (ACS) National Meeting, Anaheim, CA, March 30, 2011.

Heldebrant DJ, PK Koech, JE Rainbolt, JJ Strohm, F Zheng, and MD Bearden. 2010. "Chemically Selective Gas Sweetening Without Thermal-Swing Regeneration." Presented by David J. Heldebrant at the 241st American Chemical Society (ACS) National Meeting, Anaheim, CA, March 29, 2011.

Heldebrant DJ, PK Koech, J Zhang, CJ Howard, JE Rainbolt, CJ Freeman, and MD Bearden. 2011. "CO_2 Binding Organic Liquids *(CO_2BOLs) for Industrial Gas Purifications." Presented by Dave Heldebrant at American Chemical Society (ACS)-Green Chemistry Conference, Washington, D.C., June 23, 2011.

Hibbard KA, K Kleese van Dam, I Gorton, Y Liu, and AP Craig. 2010. "Computational Challenges in Integrated Regional Earth System Modeling (iRESM): Coupling Human-Environmental Systems Across Scientific, Technical and Semantic Divides." Presented by Kathy Hibbard at the Computational Challenges in Climate Conference, Napa, CA, August 31, 2010.

Hoyt DW, RVF Turcu, JA Sears, Jr, KM Rosso, SD Burton, JH Kwak, AR Felmy, and JZ Hu. 2010. "Fundamental Science Tools for Geologic Carbon Sequestration and Mineral Carbonation Chemistry:
In Situ Magic Angle Spinning Nuclear Magnetic Resonance." Presented by David Hoyt (invited speaker) at 2010 AGU Fall Meeting, San Francisco, CA, December 14, 2010.

Hoyt DW, RVF Turcu, JA Sears, Jr, KM Rosso, SD Burton, JH Kwak, AR Felmy, and JZ Hu. 2011.
"In Situ Magic Angle Spinning NMR for Studying Geological CO_2 Sequestration." Presented by David Hoyt at 241st American Chemical Society (ACS) National Meeting, Anaheim, CA, March 29, 2011.

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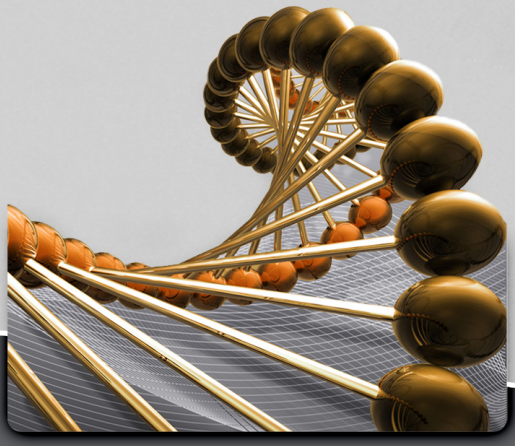

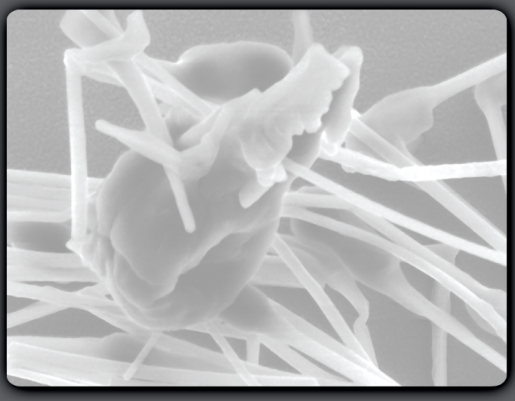

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