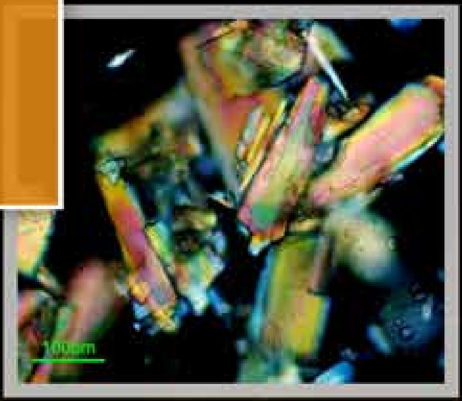
Laboratory Directed Research & Development

2012 Annual Report

at Pacific Northwest National Laboratory



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PNNL-22324

Laboratory Directed Research and Development Annual Report

Fiscal Year 2012

March 2013

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

Pacific Northwest National Laboratory
Richland, Washington 99352

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Laboratory Director's Message

The mission of Pacific Northwest National Laboratory is to transform the world through courageous discovery and innovation. Every day, PNNL scientists and engineers set out to fulfill the promise of that mission by advancing scientific discovery and delivering critical solutions to the challenges that face our nation. The science and technology we work with, create, and improve upon inspires and enables the world to live prosperously, safely, and securely.

Our investments in Laboratory Directed Research and Development are essential to our ability to realize this mission and advance our strategy. LDRD investments help us nurture science and technology capabilities while capitalizing on the breadth and depth of talent which our staff possess. This report describes how we conduct our LDRD program in compliance with DOE objectives and guidelines. We use rigorous internal and external peer review to maintain the scientific value and soundness of the research enabled by our LDRD program.

With great pride in our researchers' accomplishments, I present PNNL's Fiscal Year 2012 Laboratory Directed Research and Development Annual Report.

Michael Kluse
Director, PNNL

Advanced Sensors and Instrumentation

Advanced Environmental Sampling Technology for Safeguards and Proliferation Detection

Norman C. Anheier, Jr.

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.

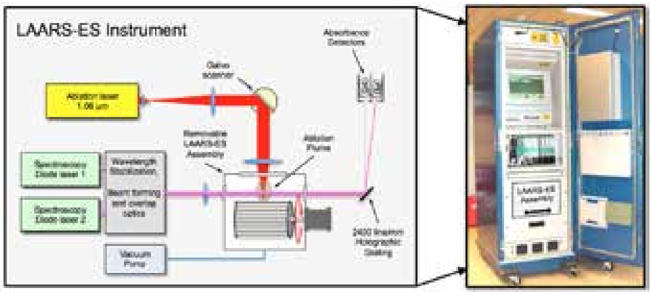
Environmental sampling is a critical verification tool for implementing safeguards and detecting proliferation activities. Under formal agreements, safeguards inspectors are granted access to nuclear sites to collect samples. Proliferation detection and verification of peaceful nuclear activities are 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 and destructive assay (DA) 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 can be used in a purpose built configuration to perform unattended near real-time monitoring of large enrichment facilities.

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 (this task was completed in FY 2009).

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 laser ablation, absorbance ratio spectrometry (LAARS) for undeclared enriched uranium detection and bias defect measurement 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 on the first project task included evaluating additional new materials for increasing the collection efficiencies of key analytes of interest that are 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.

In FY 2012, we continued to develop a Raman and fluorescence spectroscopic reference library for uranium containing compounds using the optical microscopies developed in FY 2011. A series of both uranium containing ore samples (standard reference material purchased from New Brunswick National Laboratory and the Canada Centre for Mineral and Energy Technology) as well as synthetic uranium containing compounds were acquired. The acquired samples were analyzed using BET gas sorption analysis to determine particle size distributions,



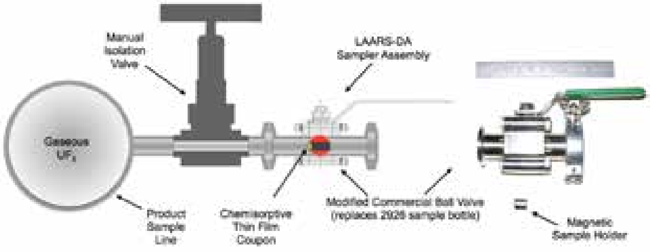
The LAARS-ES instrument used to analyze uranium enrichment in collected environmental samples. After sample collection, the stand-alone environmental aerosol sampling system is inserted into the LAARS-ES instrument for rapid uranium particulate sample assay. The LAARS-ES instrument can be designed for deployment within a standard IAEA instrument rack.

XRD for phase identification and quantification, Raman spectroscopy and fluorescence spectroscopy. The developed spectral library was used to demonstrate our ability to identify uranium compounds in mixed samples.

Under our third task, we evaluated the feasibility to adapt the PNNL-developed LAARS into a uranium enrichment facility safeguards technology. During FY 2012, the LAARS-ES deployment scenario was updated to feature a stand-alone aerosol collector based on a rotating drum impactor (RDI). LAARS-ES aerosol collectors are secured in tamper-indicating enclosures and staged at strategic locations throughout the GCEP. The collector drums are then retrieved by inspectors during onsite inspections and inserted into the LAARS-ES instrument for immediate assay.

This year, LAARS-ES experimental studies characterized prepared uranium particle samples. This study evaluated the effects of heavy sample loading and particle retention on the surface of the substrate. The RDI nozzle was redesigned to provide laminar flow within the nozzle and uniform velocity across the nozzle exit, with the goal of improving small particle capture efficiency. The particle size distribution captured by impaction is determined by the flow rate through the RDI and by the impactor nozzle outlet width and the gap between the rotating drum and nozzle. Simulation results, using a 0.25-mm nozzle width and 2-mm gap between the nozzle and drum, suggested > 90% capture efficiency down to 100 nm particle diameter at 20 LPM. The RDI performance was characterized using hematite (density 5.3 g/cm^3) aerosols having a 2.3 µm size distribution mean. The particle capture efficiency was characterized using an aerodynamic particle sizer to measure the RDI inlet and outlet particle size distributions. The collection efficiency for submicron particles is significantly improved (>65% at 0.5 µm) compared to the previous design.

A new LAARS application, LAARS-DA, was also evaluated. LAARS-DA offers on-site enrichment DA sample collection and bias defect measurement. DA samples are collected using a custom sampling device attached to a conventional sample tap. A chemisorbent film captures a few micrograms of gaseous UF_6 in just minutes. The collected DA sample is then analyzed onsite using the LAARS-DA instrument. DA results are determined in a matter of minutes at sufficient accuracy to support reliable bias defect conclusions while greatly reducing DA sample volume, analysis time, and cost.



The LAARS-DA sampling assembly shown attached to a conventional gas centrifuge enrichment plant (GCEP) sampling tap. The sampling assembly is based on a modified commercial vacuum ball valve.

Studies were conducted on thin film NaF sorbent materials that were demonstrated to have excellent UF_6 chemical trapping properties. LAARS-DA measurements produced strong absorbance signals and excellent abundance accuracy on a sample that contained only 5–15 µg total uranium.

The Task 1 Raman and fluorescence uranium study resulted in two papers published in FY 2012. Significant Task 3 technical progress was reported through several publications and presentations, including the following: 1) two papers were prepared and presentations delivered to the 53rd Annual INMM Meeting in Orlando, FL, 2) an invited papers was published in the *Journal of Nuclear Material Management*, and 3) a technology brief titled “NIS Uses Cutting-Edge Science and Technology to Advance the U.S. Nonproliferation Mission” was published in the NNSA Office of Nonproliferation and International Security Highlights publication.

Advanced Surface Mass Spectrometry for Characterization of Explosives

Christine Mahoney

> ***Our government is always in need of precise tools that can rapidly and accurately characterize explosive compositions. At PNNL's Environmental Molecular Sciences Laboratory (EMSL), we have state-of-the-art facilities containing a unique suite of analytical tools, some of which are not located anywhere else in the world. Developing these facilities and tools for national security interests will help our government both prevent and respond to terrorist acts in a timely manner.***

We intend PNNL to be a center of excellence in addressing problems relevant to national security. As such, we are currently developing several novel methods available only through EMSL, a state-of-the-art PNNL instrument user facility, for national security applications. Previous results indicated that signatures of C-4 samples from around the world could be distinguished from one another using imaging mass spectrometry. This study highlighted time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a powerful chemical imaging forensics tool for direct characterization and differentiation of explosive components (trace and bulk). It was shown that ToF-SIMS could readily differentiate between C-4 samples of varying origin based on their explosive and additive compositions. However, only 3 samples were analyzed in this work. Continuing on this theme, 17 well-characterized composition C-4 explosive samples were obtained and used as a model system for method development and advanced statistical analysis using a Bayesian integrated statistical analysis approach. Preliminary results indicate small compositional variations between C-4 samples can potentially be used in combination with robust data analysis procedures for categorization of C-4 samples. Most importantly, an infrastructure has been developed for future collaborations between EMSL and the National Security Directorate (NSD) at PNNL, a relationship particularly beneficial for the integrity of our national security.

We are currently developing several novel instrumentations both at EMSL and throughout PNNL for simultaneous elemental and molecular characterization of materials of interest to national security. These methods include ToF-SIMS, x-ray photoelectron spectroscopy (XPS), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), nano-desorption electrospray ionization mass spectrometry (nano-DESI), inductively-coupled plasma mass spectrometry (ICP-MS), and high-throughput particle analysis with an ASPEX secondary electron microscope (SEM) and energy dispersive x-ray (EDX) spectroscopy. As a starting point, we obtained a series of composition C-4 plastic explosive samples from across the country, through collaborations with the Bureau of Alcohol, Tobacco, Firearms and Explosives. These samples are commercially available, and have been characterized extensively using GC-MS in previous work. The goal was then to use our suite of advanced metrology tools for detailed characterization and differentiation of the C-4 samples based on a combination of unique organic signatures and trace elemental compositions.

Composition C-4. Composition C-4 plastic explosive is comprised of ~90% RDX, which serves as the active explosive ingredient in sample. However, C-4 also contains many other additives, such as a poly(isobutylene; (PIB) binder, process oils, di-isoctylsebacate (DOS), or di-capryl adipate (DCA) plasticizers, HMX explosive bi-products, and many contaminants and/or species that may be unique to a particular region, source, or lot.

C-4 Sample Preparation and Method Development. Both bulk analysis and imaging microanalysis methods were developed for characterization of 17 different C-4 samples, where sample preparation methods were optimized for each method utilized:

- Bulk Characterization Methods (e.g., ESI-MS and ICP-MS): The entire material was dissolved in a solvent, such as THF or acetonitrile before analysis.
- Imaging Microanalysis Methods (e.g., ToF-SIMS and nano-DESI): A nanoimprinter was used to dry transfer material directly to a Si wafer substrate by serving as a constant pressure stamper. Solution cast films were also prepared by depositing 50 µl of 2% C-4 solution in THF onto 1.5 × 1.5 cm substrates.

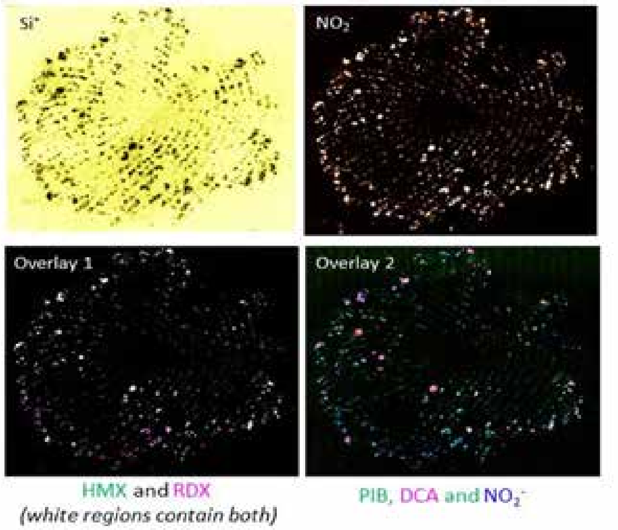
After preparation, samples were distributed to various experts for method development. A full data set was obtained from all instrumentation utilized.

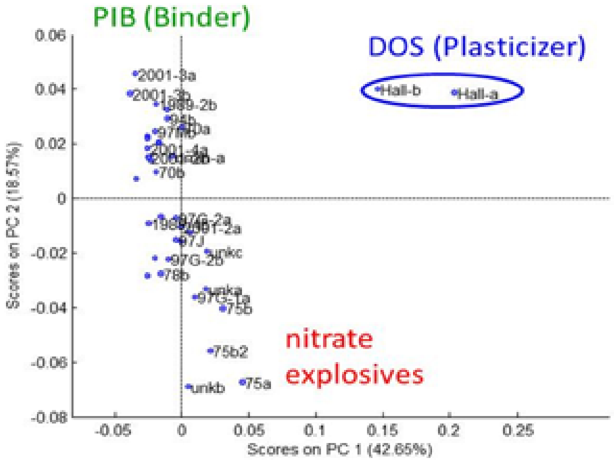
C-4 Characterization of Organic Constituents. We can organize the methods described above into organic analysis methods (such as ToF-SIMS, ESI-MS XPS and nano-DESI), and elemental/isotopic analysis methods (such as EDX, magnetic sector SIMS and ICP-MS). For FY 2012, most of our focus has been on organic characterization and analysis methods. However, methods for inorganic analysis will be introduced briefly.

ToF-SIMS is one of the primary imaging methods used for organic characterization. ToF-SIMS uses a highly focused ion beam probe (in this case, Bi_3^+) to sputter material from a surface, which is subsequently analyzed by a ToF mass analyzer. High spatial resolution mass spectral imaging of molecular, isotopic and elemental species is therefore possible with sub-micron spatial resolutions, and excellent sensitivities (ppm – ppb detection limits). Large area maps were obtained from all the C-4 nanoimprinted samples. The mass spectral data was subsequently analyzed with the aid of principal components analysis (PCA), a multivariate statistical analysis approach used to display differences and similarities in large datasets. Differences were observed in the compositions and distributions, particularly for certain commercial samples (Hall explosives) and for certain years of production (2001, 1975, and 1989 in particular). These differences were attributed to the changing compositions of PIB, DOS, RDX, and HMX.

The Hall explosives sample had the most significant differences. First, there was no evidence of HMX in the mass spectral data acquired from the Hall explosives samples, which alludes to the type of RDX processing utilized by this company. There are two primary processing methods used to manufacture RDX. The first is the rare woolrich process originally developed in England that yields RDX as the primary product. The Bachman process is much more common due to it being much cheaper to produce. This process, however, can yield up to 20% of HMX explosive as a bi-product. The Hall explosives sample was also the only sample containing peaks characteristic of DOS, as opposed to DCA for a plasticizer.

Other mass spectrometry methods employed in this study (nano-DESI and ESI-MS) yielded similar results as was observed for ToF-SIMS. Additional signatures were observed, particularly for nano-DESI but have not yet been identified. XPS is capable of determining atomic concentrations and chemical states of the elements present in the sample. XPS found significant differences for samples made in 2001, which exhibited decreases in nitrogen content relative to the other samples. This is consistent with SIMS results, showing increased binder contents in these particular samples. However, specificity of the method was insufficient for further differentiation.


a) Molecular Imaging of a C-4 Fingerprint Using ToF-SIMS


b) Principal Components Analysis of C-4 Fingerprint data from 17 different Samples

Example of C-4 characterization process using ToF-SIMS. Top panel (a) shows examples of large area molecular image analysis of a model C-4 fingerprint. Si+ (m/z 28), NO2- (m/z 46) and two molecular ion overlays are shown. Overlay 1: HMX (green, m/z 268) vs. RDX (pink, m/z 342) explosives, and Overlay 2: PIB binder (green, m/z 97), DCA plasticizer (pink, m/z 427), and nitrate explosives (blue, m/z 46). The bottom panel (b) shows the results from principal components analysis of the dataset. Each point (score) in the plot is associated with a particular sample, where different scores will have different mass spectra. For this example, the "Hall explosives" sample was significantly different from the other samples, as indicated by the very different scores. Corresponding changes in the mass spectral data indicated that there was a different plasticizer used in the production of this sample (DOS).

C-4 Characterization of Elemental and Isotopic Compositions. Elemental and isotopic analysis using a combination of SEM/EDX, dynamic SIMS (with a magnetic sector instead of ToF), and ICP-MS is ongoing. For these samples, bulk analysis of trace elemental compositions is performed with ICP-MS. Insoluble particulate matter is also being characterized with a combination of SEM/EDX and SIMS. It is expected that these experiments will be completed in early FY 2013; the complementary elemental analysis methods will significantly improve the accuracy, precision, and specificity of results.

Data Analysis. Data analysis and integration methods are a key feature of this project. Preliminary data analysis and integration approaches have been determined and will be applied to the data sets in FY 2013. Briefly, partial least squares (discriminant analysis [PLS-DA]) will be used for investigations on each individual datasets. The results of PLS-DA are ideal in that they are presented as probabilities that a particular sample belongs to a particular class. For the current example, results would report on the probability that an unknown C-4 sample belongs to a particular manufacturer or lot. These probabilities will be combined using Bayesian integrated statistics for more accurate categorization. Determinations of classification accuracy, specificity, and selectivity will be calculated, making this method admissible in a court of law. The combination of multi-modalities is anticipated to increase significantly the accuracy and specificity of the result.

Microbial Analysis. Infrastructure development for microbial forensics work at EMSL has also been started. Preliminary work has been demonstrated, where several samples of E-Coli grown in Luria Bertani and tryptic soy broth media were compared with ToF-SIMS and XPS. Preliminary data show significant differences in the resultant mass spectral data from bacteria prepared in these different media. However, a better understanding of the prominant mass spectral features is required. ICP-MS has also proven to be invaluable for trace elemental analysis of media compositions and has helped identify important mechanistic aspects of bacterial growth in different media sources.

Finally, two new capabilities being developed for analysis of microbial samples: a state-of-the-art high spatial resolution imaging mass spectrometer for analysis of single microbial cells (nano-SIMS) and a gas cluster ion beam (GCIB) source for low damage sputtering and 3-D analysis of organic and biological materials.

In FY 2013, we intend to complete our elemental analysis of C-4 and focus on data integration procedures. Once in place, these procedures likely will be used for all future forensics investigations. We also intend to utilize a high mass resolution SIMS instrument (SIMS with FT-ICR for analyzer instead of a ToF) for improved specificity and mass accuracy. At least three different publications will be submitted to reputable journals. We will then switch our focus onto microbial forensics of single cells, where we will develop our newer technologies (e.g., nanoSIMS) to address significant problems in the microbial forensics field. 3-D analysis in single cell microbial systems will be demonstrated using advanced ion beam technology. Finally, single cell proteomics will be explored with a combination of microfluids approaches and matrix-assisted SIMS (e.g., SIMS with MALDI matrices applied to surface).

Development of a Low-Cost Reliable Barometric Air Flow Station for Air-Handling Units

Darrel Hatley

This project developed a highly reliable, low-cost barometric air flow station to make economizer operations reliable through integrated design and application of emerging technologies to capture the lead in developing solutions and demonstrate PNNL's ability to address highly impactful problems with cross-disciplinary solutions.

Any serious effort focused on improving efficiency in managing the electric power grid, reducing energy consumption, or mitigating global climate change needs to consider the potential of efficiency improvements in buildings. Often, poor operation and maintenance results in equipment running in inefficient states and component failure that lead to increased energy consumption. Specifically, building ventilation (i.e., providing outdoor air) has a substantial influence on building energy consumption, occupant health, and occupant comfort or indoor environment. Despite substantial influences of ventilation rates on energy use and health, very few U.S. buildings have an integral system for measuring ventilation rates. If the average minimum rate of outdoor air supply were reduced to bring rates in alignment with the current standards and true need, savings would be approximately 0.3 quad of energy, based on U.S. Environmental Protection Agency survey results. A potential key component is the air-side economizer, a device that automatically provides free cooling to commercial buildings when operating properly, yet no effort has been initiated to solve this problem.

The project focused on developing a low-cost, highly reliable airflow measurement solution to the building equipment efficiency problem. We developed and tested a prototype hardware solution targeted at widespread overventilation when the outside air damper is at minimum position. The primary objective was to develop, test, and demonstrate a low-cost (target list price less than $500, compared with $1500~$3000 list price for existing flow station), reliable barometric-operated air flow measurement device for air handling units that would enable cost-effective ventilation rate control, which in turn would lead to significant energy savings compared to industry practices. The outcome focused on demonstrating the PNNL capability to solve this critical, well recognized problem in the HVAC industry and developing a physical prototype device.

Barometric dampers rotate from changes in pressure across the damper. The approach builds an airflow station using off-the-shelf barometric (or draft regulator) dampers and rotary sensors to measure ventilation rate. The system was tested in a typical air handler using the Research Technology Laboratory (RTL) 540 test lab and calibrated airflow stations. The damper position is sensed by a rotary sensor and the signal was interfaced to building automation system. Based on a correlation between measured airflow and damper position sensed, the outdoor air intake can be calculated. The proof-of-concept test was completed with promising results. The target market includes all air handling units with outdoor air damper installed. Compared with existing technology (i.e., pitot-tube flow station and hot-wire anemometer), this new technology provides greater cost effective, equal, or easier installation, improved maintenance, and more accurate airflow measurement solutions.

There are significant obstacles to cost-effective and accurate measurements of airflow rates. First, measurements are challenging because outdoor air intake velocities are intentionally kept low in order to minimize rain and snow from being drawn into the air handler. At these low velocities, the dynamic pressure of the moving air, which is often used to measure air speed, is only thousandths of an inch of water (a fraction of a Pascal), which is low for accurate measurements. The geometry, turbulence, and stratification of the outside air intake and its impact on velocity profiles further complicate the measurements.

A testing bed was installed in the RTL 540 with a built-in flow station and was connected to a flow hood (manufacturer's rated accuracy of ±0.5%) as the reference. The system was sealed to reduce the air leakage to a negligible level. The supply fan variable frequency drive speed was manually adjusted in small increments to allow testing over a complete range of flows. The results showed the measured airflow rate and the damper position with hysteresis between damper close (airflow decrease) and damper open (airflow increase). Hysteresis turned out to be largest issue to overcome. However, most of measured data was within range of the trended second order polynomial line with ±67.5 CFM (±5% of the maximum measured outdoor air flow rate of 1355 CFM).

The project team designed, tested, and validated the flow measurement prototype system in a real air handling unit. Damper hysteresis was the main challenges but was primarily eliminated with different damper weightings. Results demonstrated that airflow rates can be predicted using this type of device and a second order polynomial equation with results within 5% of maximum outdoor air flow error range, an industry acceptable error rate.

PN12021/2422

Forensic Analysis with Time Stamped Coincidence Sampled Gamma Radiation Spectroscopy

Larry Chilton

This project developed a novel data analysis method that takes advantage of established knowledge about the spectral features of short-lived radioisotopes and exploits changes in relative abundances over time to increase the confidence of identifications.

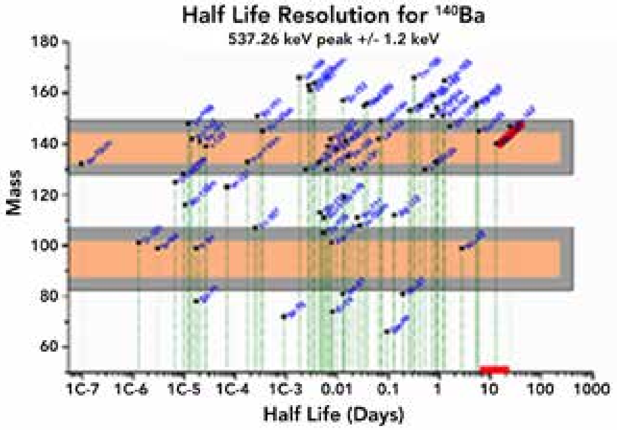
Often, cutting-edge sensors produce measurement data that require novel analysis for signature discovery and detection. This is certainly the case for the application on which we focused, which was to develop methods to detect the signatures of radio-isotopes in data collected by the a direct simultaneous measurement (DSM) instrument. PNNL compiled terabytes of time-stamped coincidence-sampled (TSCS) gamma-ray spectral data with the DSM consisting of fission product gamma-ray measurements within which valuable nuclear forensic information is contained. However, no spectral analysis tools exist to extract this important information. Of particular interests are short-lived isotopes (SLIs) and the accurate characterization of isotopes in the presence of interference.

Current state-of-the-art approaches for gamma-ray spectral analysis are designed for time-integrated spectra. As TSCS data sets are summed to time-integrated gamma spectra for analysis, the process ignores added information produced by time-stamping and coincidence-sampling. Developers and users of the DSM are confident that maximizing the time-series and coincidence-sampled data will likely yield new insight into the isotopic composition of material samples, especially for short-lived isotopes. Importantly, accurately identifying these isotopes in environmental samples supports several national security missions, including nuclear nonproliferation, forensics, and safeguards and security.

Identifying the isotopes in a fission sample is often used in forensic analysis to gain information about the origin of the material. The typical approach to the problem is gamma ray spectroscopy. The challenge is that complex mixtures contain many isotopes with the same or overlapping characteristic peaks and other ambiguous identifying features such that some isotope identifications are highly uncertain or not tractable. Traditional solutions often involve radiochemical separations of the samples into simpler mixtures, which is not optimal because the time necessary for separations may result in some isotopes decaying to point below instrument sensitivity. Also, the facility and safety requirements for radiochemical separations are significant.

We used data collected from irradiated samples with coincidence gamma ray spectroscopy to investigate differentiating characteristics of short-lived isotopes associated with their half-life and combined with their spectral features. When successful, this method decreases the amount of time necessary to resolve the contents of a complex mixture, quite possibly reducing the need for the radiochemical separation. Exploiting time series of spectra for identification and quantification of isotopes in a mixture required that the instrument efficiency and dead time be characterized. This information was then used to adjust the apparent starting quantities and half lives for isotopes of interest. The failure to make these adjustments would likely have resulted in underestimates of the initial quantity and an over-estimate of the half-life.

The dead time and efficiency for the instrument was characterized, and experimental data were adjusted for these parameters. Consequently, these data were analyzed with time-series methods to estimate isotope half-life by modeling the change in count rate over time for specific spectral features associated with the isotope of interest. The results for ^{140}Ba, ^{95}Zr, and ^{144}Ce were very encouraging, as the combination of known spectral activity channels and half-life estimation using data in time series for known present isotopes resolved the half-life within a few percent. Equally important, when the isotopes are not present, half-life estimates do not indicate their presence. As a result, two papers are being prepared for peer reviewed publication: one addresses the statistical methods developed for isotope identification, and the other presents approaches to system independent dead time estimation and correction.



Eighty-five isotopes have spectral peaks at 537 keV, but only one, 140Ba, also has a half-life of 12.74 days.

PN12033/2434

Glider-Based Passive Acoustic Detection System Capability Development

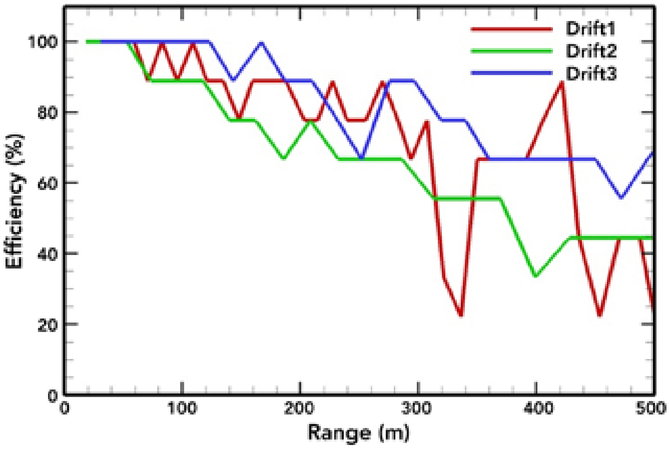
Kyle B. Larson

PNNL is exploring ways to utilize an autonomous, wave-powered sensor platform called the Wave Glider™ to help resolve critical knowledge gaps about marine mammal populations, which can be a major obstacle to offshore project citing and permitting. Benefits of this research include significantly reducing the costs, risks, and biases associated with traditional ship-based surveys as well as improving the scientific community's understanding of marine mammal populations.

Traditionally, information on marine mammal populations is gathered via shipboard or low-level aerial surveys, which have poor detection efficiency are inherently dangerous, and may be cost prohibitive. To help address these issues, researchers have begun exploring ways to couple acoustic detection technology with unmanned ocean vehicles that can essentially collect data continuously. However, significant improvements to these systems are still needed to make them a practical application, including automating data collection and analysis, systems integration, developing survey protocols, and understanding the limitations of the data.

To facilitate development of offshore wind and marine hydrokinetic (MHK) energy sources requires innovative solutions to resolve knowledge gaps on marine mammal populations (e.g., distribution, abundance, migration, and use patterns), which can be a major obstacle to project siting and permitting. The goal of this work is to advance the use of an autonomous glider-based passive acoustic detection system (PADS) for collecting data on whale populations needed to facilitate project siting and environmental permitting processes for offshore wind energy development (i.e., species presence, distribution, abundance). Currently, data are collected by trained human observers on ships and aircraft, which may be costly and can be limited by sea conditions.

Commencement of this project demonstrated the proof-of-concept for a passive acoustic detection system capable of automated detection on the Wave Glider platform. Efforts to integrate the detection system with the glider so that data can be obtained remotely were not feasible in FY 2012. Key technical goals throughout the year included 1) designing and building a prototype passive acoustic detection system, 2) developing an algorithm to conduct automated detection of southern resident killer whale (SRKW) calls, and 3) assessing the detection efficiency and range of the prototype detection system affixed to the glider.



Preliminary results of three broadcast drifts conducted in Sequim Bay, WA indicate that detection efficiency is generally ≥ 80% at distances less than 200 m.

A prototype passive acoustic detection system was designed and built in FY 2012, consisting of omni-directional, low self-noise, broad-band hydrophones, signal conditioning interface/amplifiers, a single-board computer, data processing software, energy-based detector, and two rechargeable batteries. An algorithm was developed to perform detection of SRKW calls using signal-to-noise ratio (SNR) methodology, which employed real-time loop recording that allowed the system to listen continuously and provided the ability to record the full duration of candidate whale calls. Ultimately, this process ensured adequate recording quality for post-processing verification of detections.

Preliminary laboratory and field tests were conducted to improve algorithm performance and detection thresholds before assessing detection performance on the glider. Additional improvements were made by modifying the signal conditioning hardware to optimize SNRs. Detection performance (efficiency and range) was evaluated by broadcasting recordings of SRKW calls from a silent drifting boat while the glider attempted to hold position. Preliminary results of these tests suggest the average effective detection range (i.e., the range in which detection efficiency was at ≥ 80%) is approximately 200 m and the maximum detection range is approximately 600 m.

We were able to demonstrate proof-of-concept of automated whale call detection successfully on the Wave Glider platform. The system's ability to detect SRKW calls exceeded its expected detection range, indicating that there is good potential for improving detection range. In addition to integrating the detection system to operate within the design constraints of the Wave Glider such that it can function as a fully autonomous survey vehicle, this situation is ultimately required in order for this application to be a useful tool for monitoring marine mammal populations.

PN12036/2437

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

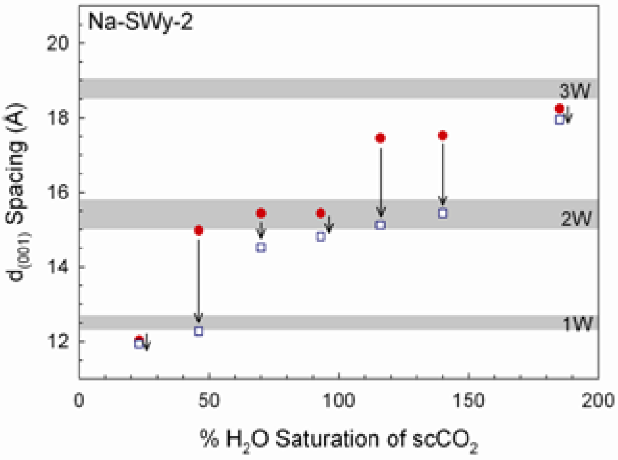
H. Todd Schaef

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 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 well-accepted conceptual model, most research on flow, transport, and chemical reaction processes has remained in aqueous-dominated geologic systems, which will not represent the vast majority of rock volume where $scCO_2$ is stored. Moreover, recent PNNL work indicates that chemical reaction processes between water solvated in the $scCO_2$ 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 the project, a high pressure reactor was designed, fabricated, and tested at pressures and temperatures relevant to geologic sequestration. In the project's second year, we conducted testing on pure minerals, including brucite, montmorillonite, and forsterite. Activities occurring in year three focused on integrating experimental measurements with complementary techniques including isotopic labeling and molecular dynamic simulations.



In situ HXRD graphs depicting interlayer spacing changes when exposing variable hydrated sodium saturated montmorillonite to $scCO_2$ at 50°C 90 bar.

In FY 2012, we used in situ HXRD to examine the carbonation of a pyroxenoid mineral, wollastonite [$CaSiO_4$], in contact with wet $scCO_2$ at pressures (90, 125, 160 bar) and corresponding temperatures (50°, 55°, and 75°C) selected to simulate reservoir conditions. Exposing wollastonite to anhydrous $scCO_2$ resulted in no detectable carbonation. However, the addition of water above ~50% saturation level of the $scCO_2$ resulted in partial carbonation through the formation of calcite, detectable within a few hours at all conditions. Increases in water content correlated to increases in carbonation. Tests conducted below the 50% water threshold did not produce detectable carbonation by the *in situ* XRD method. Oxygen-18 enriched water was used to track mineral surface hydration processes occurring in the wet $scCO_2$ environment.

Reaction processes occurring with clay minerals (montmorillonite, kaolinite, and chlorite) common to caprock formations were explored through varying amounts of dissolved water in the $scCO_2$. These experiments suggest a high degree of stability for kaolinites and chlorites when in contact with wet $scCO_2$; no detectable structural changes were detected with the *in situ* HXRD technique. However, characterized by their ability to accept water into their interlayer, montmorillonite clays proved dynamic when exposed to $scCO_2$. Depending on the interlayer cation and hydration state, exposure to anhydrous $scCO_2$ produced a

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structural change resulting in measurable minerals volume changes. Lower hydration states (~1 water of hydration) were least affected when exposed anhydrous $scCO_2$ under conditions relevant to geologic sequestration. By contrast, montmorillonites containing 2 or 3 layers of hydration were most susceptible to dehydration process when in contact with anhydrous $scCO_2$ and often produced decreased clay volume.

These types of experiments continued to provide a database for predicting potential permeability changes occurring to caprock seals. In some environments, initial exposure with anhydrous $scCO_2$ will cause dehydration of the interlayer water and subsequent collapse of interlayer spacing. However, the process is reversible, and following uptake of water by the $scCO_2$ fluid, swelling of clays will occur and thus help maintain caprock integrity. Moreover, through molecular dynamic simulations, it appears the presence of wet $scCO_2$ facilitates the incorporation of water into the interlayer and leading to its expansion. 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 2013 are designed to maximize exposure and promote the *in situ* capability primarily through finalizing publications and conducting limited high-pressure experiments on second generation designs. Immediate efforts will focus on presenting at the Greenhouse Gas Conference (GHGT11) in Kyoto, Japan in November and completing the final manuscript on interactions between montmorillonites and water bearing $scCO_2$. To expand this in situ HXRD capability, a second generation cell has scheduled for final testing before project end.

Low Frequency Electromagnetic Interrogation Techniques for Container Content Signature Detection

A. Mark Jones

This project performed a simulation-based investigation of the use of low-frequency electromagnetic signals to detect concealed radiation threats in large, closed metal containers via the impedance signature produced by eddy currents induced in conducting shielding materials. Depending on the concept of operations and container physical and electromagnetic properties, it was determined that this technology has the potential to enable rapid volumetric inspection of containers to assist with detecting illicit or diverted nuclear materials.

Research previously conducted at PNNL has demonstrated that the low frequency electromagnetic (EM) response of a sealed nuclear weapons component 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.

This project explored the use of low-frequency EM energy to interrogate large metal containers that contain radiation threats shielded by conducting materials. Examples of conducting radiation shielding materials are lead, tungsten, and iron. Unknowns included the sensitivity of the signatures to variations in container and internal object size, composition, and geometry. We evaluated frequency ranges and sensor configurations which maximized the response of the coil system for various inspection scenarios. Because experimental characterization of a complete set of these orthogonal parameters is unrealistic, we employed advanced finite element electromagnetic field simulation software to investigate numerous detection configurations. 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 material storage container. Excellent agreement was obtained between the simulated and measured results.

The electromagnetic field distribution and coil impedance response produced during a given container interrogation is dependent upon multiple factors such as the position, orientation, size, shape, surface area, and metal type of the internal contents. From the complex interaction between these variables, it is difficult to formulate a single figure of merit that can be used to describe the sensitivity of the coil method for general combinations of metal containers and contained objects. The ability to efficiently perform systematic investigations of these system parameters using simulation software is a key enabler in understanding how the technology can be applied.

For coil geometry, simulation results showed that encircling coils yielded better overall detection of centrally located objects inside large containers than pancake or surface coil configurations. In frequency range, the magnetic field penetration of container walls occurred for frequencies under 2 kHz for the majority of configurations analyzed. With container penetration, metal containers can be constructed from materials that exhibit magnetic or non-magnetic properties. A magnetic container exhibits a high magnetic permeability that significantly decreases the ability of magnetic fields to interact with contained objects. The container wall thickness is another factor that affects field penetration, and the skin depth equation can be used to understand field penetration as a function of frequency and both container wall thickness and electromagnetic properties. In contained object geometry, the largest coil responses are produced by objects with a high electrical conductivity, high magnetic permeability, and large cross-sectional area along the direction perpendicular to the primary magnetic field. The interaction with the object is governed by the physics of Foucault currents induced on a conducting object.

An extensive set of EM simulations was performed 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 3D models were analyzed for 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. As an example, a detailed study of detection sensitivity was conducted for lead and carbon steel shielding materials located in the center of an 8 ft × 8 ft × 10 ft IMCC. The shielding material was represented by a solid rectangular prism with a height and width of 1 ft and a length ranging from 1 ft to

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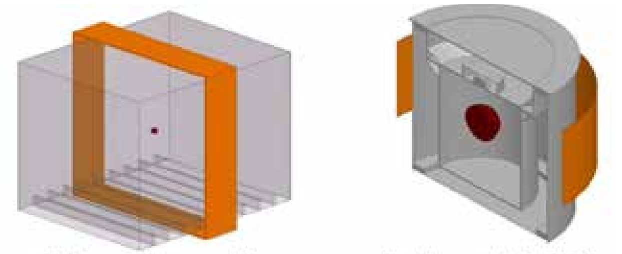
4 ft. To facilitate the simulation study, the container geometry was simplified with smooth steel in place of corrugated steel walls; corner posts and door latches were not included; and gridded beam floor construction commonly used in cargo containers was included. The goal was to determine if the introduction of materials during transit could be detected by comparing coil responses measured at the origination and destination ports.

Results determined that an optimized encircling coil could be used theoretically to detect mass changes on the same order as those expected to conceal introduced illicit nuclear material. Statistical noise levels were quantified using small-scale coil measurements with a DOE-STD-3013 container and applied to noiseless simulation results to estimate the smallest detectable changes in object mass. The effects of expected temperature differentials at the two measurement sites on container and material electrical properties were also studied. Temperature changes were found to impose significant limitations on detection sensitivity unless this factor was addressed, and several techniques were proposed to compensate for this effect. Simulation studies also investigated the response of encircling coils used to inspect metallic and composite air cargo containers that contain metallic shielding objects. We confirmed that the trend toward adopting metal-framed composite air cargo containers increases the detection sensitivity of the coil method.

We also completed a study to determine if the coil signature could be used to detect threats with small metal components inside large steel drums. Steel drums are of high interest in security screening since sealed metal drums containing high-value liquid or powder cargo are difficult to screen for threat items. The coil response for various threat surrogates placed in different orientations inside a 30-gallon steel drum was quantified using simulations and measurements. For many items explored during the study, background noise levels and container property variations precluded detection via the coil method. The use of non-magnetic stainless steel drums would improve detection sensitivity; however, due to material costs, the vast majority of metal drums are constructed from carbon steel.

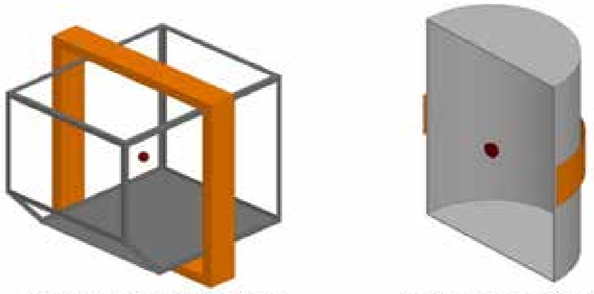
A method for increasing the coil method sensitivity was proposed, simulated, and verified using laboratory experiments. This method introduces a resonance at a frequency in the operating bandwidth by adding capacitance to the coil system. Sensitivity improved by at least one order of magnitude at the resonant frequency compared to the non-resonant coil method. Measurements were performed using this method on the AT-400R nuclear storage container and an Excalibur munitions storage container.

We accomplished our intended tasks on this project, which included progress in arms control treaty verification applications. The results of our simulation study of coil response for a hypothetical nuclear material storage container as a function of a variety of operational parameters were accepted for publication in the fall 2012 *Journal of Nuclear Materials Management*. We presented technical results coupled with policy considerations at the 53rd Institute of Nuclear Materials Management conference in July 2012. This publication outlined the potential for the coil method to be used for verification of declared forms during plutonium disposition and prevention of diverted material in the chain of custody. For example, simulation results demonstrated that it is possible to distinguish between different metals and oxides as the oxide forms do not interact with the applied field and the result is the same as an empty container, which is complementary to radiation detection methods that cannot distinguish between oxide and metal forms. In addition, because magnetic fields do not interact with the material nuclear structure, the coil method reveals no information about the isotopic nature of disposition materials.



Carbon steel intermodal cargo shipping container

Stainless steel AT-400R nuclear storage container



Aluminum-framed composite air cargo container

Stainless steel nuclear dismantlement container

Representative finite element model geometries used in coil sensitivity studies. Sphere diameter is 10 cm in all models shown.

During the weapons dismantlement process, it will likely be necessary to verify that large metal containers are actually empty and contain no nuclear material intended for diversion from the chain of custody. Radiation measurements alone may be insufficient for verification since the nuclear materials could be concealed through the use of shielding materials. Simulation results for a 5 ft tall stainless steel container demonstrated that the EM coil method can detect the presence of lead material in amounts necessary to shield a substantial quantity of nuclear material.

In summary, this project performed fundamental research to investigate the use of the induction coil method for a variety of important national security applications. We combined powerful simulation studies and appropriate lab measurements to gain valuable insight into the capabilities and improvement of the inspection method. Project results demonstrated a methodology to enhance PNNL's capabilities for supporting security screening objectives and arms control treaty verification.

Low-Noise, Low-Background Electronics

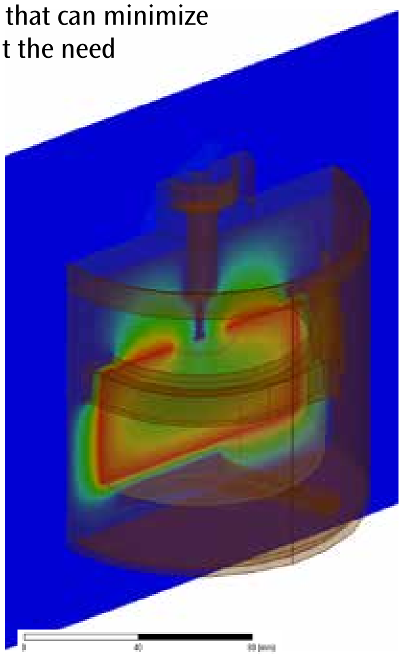
Brent A. VanDevender

This project will establish a PNNL world-class capability for low-noise low-background electronics to support the ultra-sensitive nuclear measurements often demanded by national security and basic science applications.

Electronics noise restricts the sensitivity and accuracy of radiation detection systems but can be abated by careful design and layout of electronic circuits following well-known principles. However, these practices alone are insufficient to meet much less exceed the state-of-the-art. Attention must be paid to geometries and materials in the environment in which the detection system operates. Any electrical conductors in the environment will result in stray capacitance that couples into the circuit in ways that can defy the intuition of even the most seasoned electronics engineer. These parasitic capacitances are a source of noise at best, and they frequently result in the complete malfunctioning of circuits (e.g., feedback amplifiers driven into oscillation). The problem is exacerbated if any of the stray capacitance results from electric fields in dielectric material.

The sensitivity of nuclear measurements is often limited by levels of electronic noise and/or intrinsic radioactivity in construction materials of detector systems. This is especially true in contemporary national security and basic science applications, where signal events of interest may be small and/or very rare and thus easily obscured by noise and backgrounds. Expertise in low-noise analog electronics design germane to radiation detectors is increasingly scarce, especially in the United States. We will remedy this situation by building a comprehensive capability at PNNL to support low-noise analog electronics design for radiation detector systems. We take a system-level view of this capability that extends from the initial charge creation in sensitive detector elements, through the amplifier electronics to digitization for data acquisition. PNNL is a world leader in the production and use of ultra-low background materials for the construction of detector systems, and we will extend that capability to the electronics used near sensitive detector elements.

Two immediate problems to meet our low-noise low-background electronics goals are identified: stray electrical capacitance in germanium detector cryostats and poorly understood performance of ultra-low background proportional counters. The noise in a typical amplifier used with germanium detectors increases with increasing capacitance at its input. In addition to capacitors that are part of the amplifier circuit, this includes the capacitance of the detector itself, and the stray capacitance of the grounded conductors used as structural elements of the system. Advances in detector and electronics technologies have reduced the first two sources to such a level that the latter source can no longer be neglected in the effort to reduce total noise contributions from capacitance. To account for this, we have developed the capability to model the electrical capacitance of realistically detailed detector systems with finite-element analysis software. Electrical modeling is closely coupled to the mechanical design process for a fast virtual-prototyping cycle that can minimize stray capacitance without the need to build and test many iterations of an expensive system.



The electic potential inside a PNNL-designed low-background low-capacitance germanium detector cryostat on a plane through the central axis (blue = ground, red = high voltage).

Electric field modeling also supports the analysis of ultra-low background proportional counter (ULBPC) performance. ULBPCs developed to detect 37Ar in support of on-site inspections for verification of nuclear test-ban treaties have a lower efficiency than expected. The cause is hypothesized as being complicated electric field structures near the ends that were not considered in the original design. Field modeling is being used to inform future designs in a similar virtual prototyping cycle.

With our team increasing its background in electronics for radiation detectors and improving the history of capability development, we will continue to address immediate challenges while continuing to build capability in FY 2013. Our long-term capability consists of the equipment required to outfit an electronics laboratory. We are establishing a dedicated hardware test stand for evaluating noise sources in part through developing support of low-capacitance, low-dielectric-loss design through field modeling. In addition, we will further implement the integrated software framework to serve slow control, data acquisition, and analysis functions for the test stand.

PN12046/2447

Neutron Signature Detection Requirements for Identifying Warhead Configurations

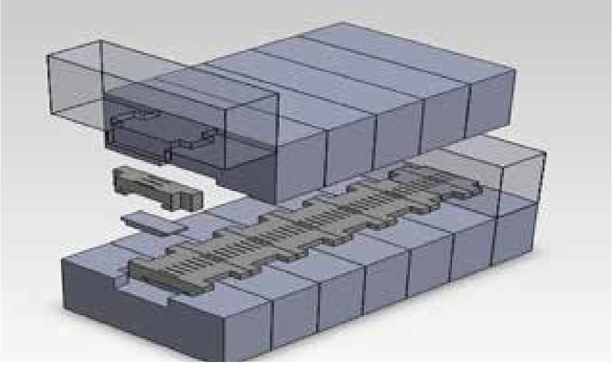
Jacob M. Benz

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 project work in FY 2011 focused on the construction of detailed MCNP5 models for five different U.S. weapons types, which have been placed within various shielding materials and configurations to determine their effect on the emitted neutron spectrum. Careful analyses and many discussions with experts were used to develop a modeling matrix to track the many potential scenarios and configurations of interest.

The matrix was then used in conjunction with change detection software to determine the potential of using this mechanism for template matching or type differentiation. The weapon types and shielding configurations were then put through a series of comparisons, resulting in a stoplight chart representing the degree of confidence in type differentiation for a variety of real-world detectors. 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 reliably to distinguish one configuration from another. In the remaining cases, differences in shape of the detected fast-neutron energy spectra clearly distinguish the configurations.



3D design of the passive neutron spectrometer showing the flexible placement of the TLD chips as detection media.

The focus of FY 2012 was to design, fabricate, and characterize a passive neutron spectrometer. PNNL partnered with a mechanical engineering design team to design and fabricate the spectrometer. Upon delivery, a series of measurements were performed to begin characterization of the spectrometer. The sources included bare Cf-252, D2O moderated Cf-252, and PuBe. This range of sources was chosen to determine whether the spectrometer could distinguish between fission, thermalized, and (a,n) neutron spectra.

The design utilized TLD chips as the detection media in the spectrometer. Therefore, detector response is given as a total dose or dose equivalent deposited in each TLD chip. Additionally, the design allowed for the flexibility in the placement of the chips to accommodate a neutron field of varying energies (0.02eV to 20MeV). Chip locations are chosen in such a way that each chip receives a minimum of 10mrad (100mrem). This threshold minimizes potential readout uncertainties being introduced during readout. A comparison of modeled to measured configurations agreed well in the overall shape of the response. Outstanding issues related to the conversion of energy dependent dose-to-dose equivalent created a difference in the magnitude of the measured to modeled dose responses.

Final analysis of the effectiveness of this neutron spectrometer to discriminate between declared configurations was then put to the test. Change detection was performed on the measurement results and also the various weapon configurations modeled in FY 2011 by inserting the actual characterized detector response of the neutron spectrometer. Results indicated that it was possible to discriminate sources of varying neutron spectra after a reasonable measurement time.

PN11057/2379

Novel Detector Configurations

Marty Keillor

This project sponsored the production of a wide range of new radiation detection concepts that have the potential to lead to significant sensitivity improvements over the existing technology. The objective was building capability in existing PNNL strength areas and expanding our repertoire of highly sensitive radiometric measurement systems.

Across a broad spectrum of basic and applied science, ultra-sensitive measurements of radiation are used to answer critical questions. In the arena of neutrino properties and dark matter, as few as several events each year in a large experiment hold the key to discovery and observation. In fields such as nuclear treaty monitoring or environmental carbon cycle detail probing, ultra-sensitive measurements offer the ability to obtain answers from smaller samples and provide a more precise quantification of measured indicators. Specifically, the world's most sensitive nuclear measurement systems rely on techniques developed to reduce or discriminate unwanted background signals. This project maps a near-term approach for detector science, focusing on the set of challenges that must be overcome to enable a new generation of sensitivity and diversity of application for ultra-sensitive measurements.

Recently, PNNL pursued a relatively focused set of ultra-sensitive radiometric measurement technologies. For radiopure materials, these include methods development for the production of ultra-pure copper and the assay of a limited selection of commercial materials. For detector technology production, successful research projects developed single-crystal cryostats and arrays of high-purity germanium crystal, ultra-low-background gas proportional counters, new glass scintillator materials, and cadmium zinc telluride arrays. In addition, β–γ coincidence detection systems for sensitive measurements of gas samples (e.g., xenon) have been a focus area, along with the development of sophisticated gas separation and purification systems to prepare samples for measurement.

This one-year research effort combined a literature study of recent advances in radiation detection techniques with an analysis of PNNL strengths and weaknesses in the arena of ultra-sensitive radiometric measurement technologies. The effort sought to identify those areas where PNNL was poised to move the state-of-the-art forward; an effort was also made to recognize areas of weakness where targeted hiring could provide a significant boost to PNNL capabilities.

We examined a wide variety of potential near-term research paths to enhance PNNL capabilities in ultra-sensitive radiation detection. The effort identified promising new detector developments that capitalize on existing PNNL detector technology strength areas: intrinsic germanium spectrometers, ultra-low-background gas proportional counters, scintillators, coincidence systems (e.g., germanium arrays, β–γ systems), and cadmium zinc telluride arrays. Research also considered areas ripe for progress to improve availability of ultra-pure materials. We anticipated reaping several of the following benefits from this study: 1) promising technologies that represent opportunities for further sensitivity improvements; 2) prioritized research topic areas for consideration of near future funding; and 3) initial performance modeling for the most promising candidate detector technologies.

This project sponsored the production of a wide range of radiation detection concepts with the potential to lead to sensitivity improvements over existing technology. Individual researchers developed 5–10 page concepts with background information and the outline of a new proposition. The focus of these studies was on advancing existing technology or configuring existing technology in new ways, rather than developing fundamentally new detectors. Brainstorming sessions were held to consider the concepts under development and to provide a broader view of each problem.

Deliverables completed under the project included the production of an FY 2013 Call for Proposal text in the area of ultra-sensitive measurements systems. Ten proposals were submitted based on that call. A total of 3 ideas were considered to require further concept development, 6 were judged to have significant potential for funding through other venues without LDRD investment, and one was selected for LDRD funding by the laboratory through its normal review and approval process. The second deliverable is a final report detailing the concepts developed under this project, which is in progress.

One significant outcome of this effort was determining that the method pursued resulted in concepts that were mainly evolutionary, taking the next step in the strength areas of our researchers. While this generates useful research topics, it does not tend to produce the preferred higher-risk, higher-reward research projects. Brainstorming on this topic led us to a new approach that we believe will assist in stimulating innovative thought and intriguing new radiation detection concepts. This method, which includes documenting the weaknesses of current detection technologies along with the desired improvement, will be pursued both in the final report of this project and in the coming year by laboratory management.

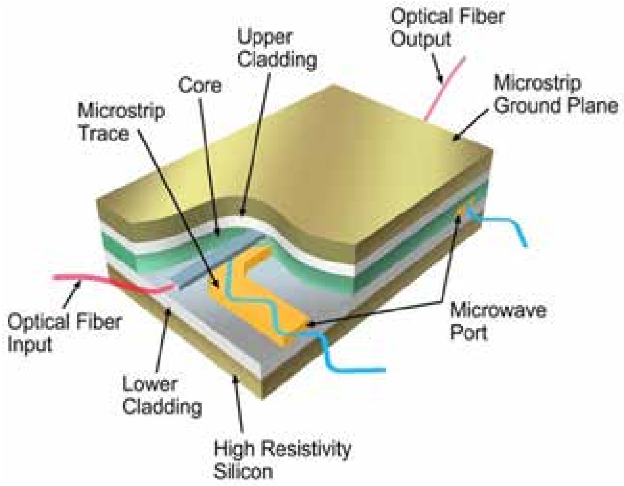
PN12056/2457

Optical Upconversion for Passive and Active Millimeter and Terahertz Imaging

Douglas L. McMakin

> ***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 signals can penetrate many obscurants opaque to optical imaging but offer lower spatial resolution than optical approaches. Synthetic aperture imaging can increase spatial resolution by exploiting a large baseline array of small antennas but its implementation is challenging using conventional millimeter-wave technology. Using optical upconversion, synthetic aperture imaging exploits the use of compact and low-loss telecom fibers (1000× 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 can be used for wideband radio frequency (RF) modulation to increase resolution of fielded active systems such as the PNNL-developed millimeter wave imaging portal employed at many airports. Polymer-based modulators also offer better performance (wider modulation bandwidth into the sub-THz region and lower V_π), potentially lower cost, simpler fabrication methods as well as compatibility with integrated circuit technologies compared to the more traditional crystalline lithium niobate materials. More importantly, PNNL boasts staff with expertise in fabrication of electro-optical polymer materials and devices.



Graphical rendering of our polymer-based electro-optical modulator design with RF microstrip input.

The project goal was to design, build, and demonstrate an optical modulator to upconvert microwave energy directly into an optical signal representation. 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 sought to have developed a polymer system (cladding-core-cladding) suitable for an active electro-optical modulator, fabricated a phase modulator, and demonstrated the upconversion of microwave signals to their optical representation under modulation of an RF signal. The project would demonstrate the use of RF modulator components that permit all-optical processing of microwave and millimeter-wave signals injected into the RF waveguide. The parameterized RF signal would faithfully preserve the relative power, spectral response, and polarization state of the incident beam. The ability to generate a stable optical carrier enables stable synthetic aperture systems that can make possible mobile video-rate passive imaging systems with reduced size, weight, and power. Originally, we sought to design our modulator at 94 GHz but changed to a 10-GHz design in order to use lower cost RF components and test equipment.

In FY 2011, we selected and developed a thermoset polymer for the core with high chromophore loading, and chose a compatible thermally-cured epoxy for the cladding. We also designed a passive optical waveguide using numerical modeling and demonstrated single mode wave guiding in one dimension in fabricated polymer waveguides using our optical waveguide characterization facility.

During FY 2012, we demonstrated lateral and vertical confinement with single mode operation using an inverted rib design for lateral confinement. The rib was embossed using a PDMS stamper for rapid processing turnaround but closer evaluation showed excessive optical loss per cm due to unacceptable roughness in our thermoset core material. This was due to its viscous nature and reluctance to form a smooth layer by spin casting. Therefore, we substituted SU-8 doped with DR19 in a guest/host system and proceeded to design a novel structure (resulting in a patent disclosure) using an inverted RF microstrip waveguide with S-bend. To form the RF waveguide, we developed a process to pattern sputtered silver on polymer followed by plating to achieve the required thickness of 4 µm. Additionally, we developed a process to pole our active polymer layer using

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the corona method, and demonstrated the expected resultant birefringence using ellipsometry and prism coupling. Poling is required to align the as-deposited chromophore molecules to elicit their non-linear optical behavior in the presence of the polarized optical field and modulated electric field produced by co-propagating RF signal in the microstrip. We also obtained RF test probes to inject test signals into the micron-scale RF waveguide from RF signal generators and demonstrated their use and designed a test method using a length of test RF microstrip.

By project's end, we demonstrated the building blocks of each step necessary to fabricate the polymer electro-optical modulator: a core/cladding system, inverted rib waveguide design, method to fabricate the inverted rib using embossing as well as reactive ion etching, method to pattern the silver microstrip and plate additional silver to necessary thickness, method to corona pole the active layer, and test fixtures and procedures to inject the microwave signal into the device to demonstrate operation.

Regrettably, there was insufficient time once these necessary preliminary steps were accomplished to integrate all of the above building blocks into a working demonstration device. However, we established a capability to design, fabricate and characterize polymer waveguides, developed a process to obtain and fabricate electro-optically active polymer layers, pattern small featured metal patterns on polymer, corona pole to achieve optical activity, and also design and test novel RF waveguides to couple modulation into the optical upconversion device. The strong partnerships developed between team members, staff development, and new capabilities made possible by this project will undoubtedly impact future projects vital to our national security.

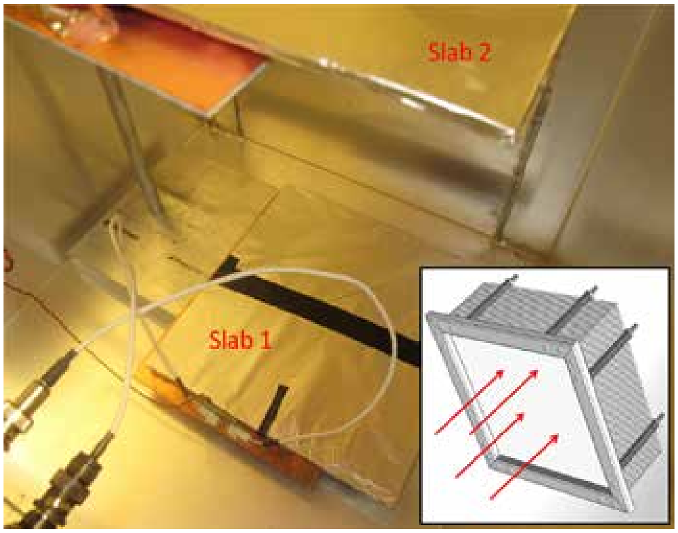
Prototype Fast Neutron Detector

Sean C. Stave

We are developing a detector with the ability to distinguish neutrons from gamma rays using a plastic scintillator, a non-volatile material that can be used anywhere.

A high-rate-capable, non-volatile detector of fast neutrons may have a role in the future of active interrogation of special nuclear materials. This detector takes advantage of the different time scales for neutron and gamma-ray interactions in layers of plastic scintillator and uses precision timing to pull the neutron signal out of the gamma-ray noise. Previous efforts used large, single pieces of plastic scintillator and focused on very fast read out of the light. Our modeling efforts show that approach to be inadequate due to pile up of multiple events and the sheer size of the detector smearing out the light signal.

Our concept utilizes dozens of thin slabs each with its own individual high speed light sensor which preserves the timing information. The small slabs have less time spread on the light collection and can individually run at high rates allowing a wider range of rates over which the detector is sensitive. Our efforts have focused on modeling this detector and testing key components in the laboratory to confirm our model predictions. We expect a proof-of-concept device that will be tested in a real beam environment by the end of the second year. The lessons learned from this project will allow a more precise determination of the path required to scale to a larger and more efficient detector.



Two thin scintillator slabs connected to MPPCs used in the initial timing and light output laboratory measurements. Both slabs are located inside of a light tight box to minimize the effect of stray light. Inset: Conceptual 20-slab design with arrows indicating incoming particles.

PN12064/2465

Modeling studies were performed using GEANT4 to investigate the best geometry for the detector. Thin slabs were settled on due to their superior performance as a group but a design using thin tubes was also studied. The tubular design had better light collection but the slabs had fewer channels of electronic readout and better timing properties.

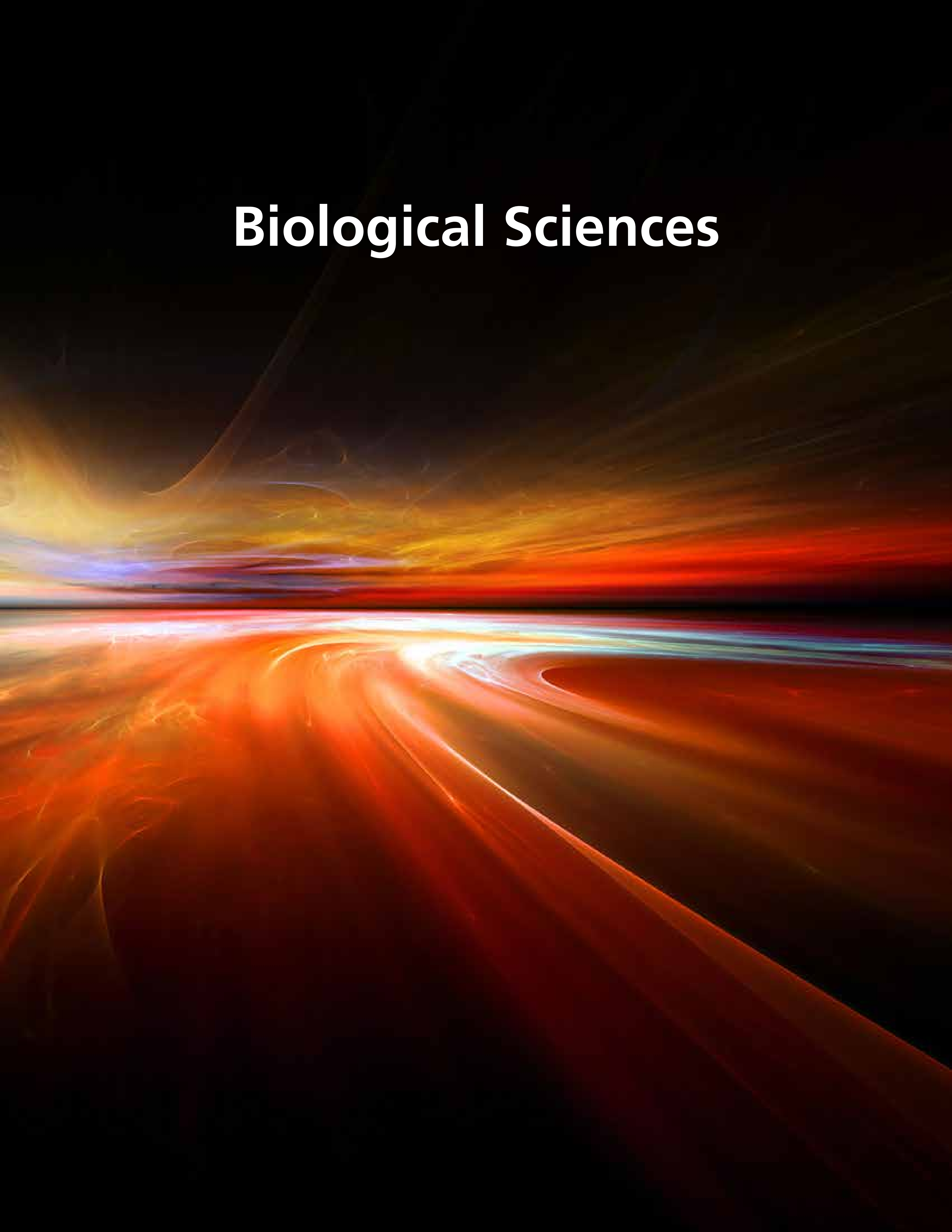
Two key properties were identified and studied: the expected light output for gamma-ray and neutron energies between 2 and 10 MeV and the timing resolution associated with the collection of that light. If the light signal is too small or the timing resolution is too coarse, the concept will not work. Due to the compact size of the slabs, small multi-pixel photon counters (MPPCs) were chosen as the light sensors. These sensors measure 3 mm × 3 mm, run at much lower voltages than photomultiplier tubes, have single photon sensitivity and have sufficient intrinsic timing resolution.

Laboratory testing was performed using two plastic scintillator slabs separated by 30 cm and a 500 MHz waveform digitizer to capture signals from the light sensors. Both gamma-ray and neutron sources were used, and testing confirmed that the timing resolution was more than sufficient (< 3 ns FWHM) and the light output was sufficient to detect neutrons with energies of 2 MeV and up.

A time-of-flight measurement was performed using the two slabs. Neutrons could be distinguished from gamma-rays based on the time between the pulses. The processing of the digital signals requires more work in FY 2013 to reduce the gamma-ray background but results are promising. Multiple cutting-edge components (MPPCs, waveform digitizers, digital pulse processing) were brought together to reduce the size and complexity of the detector while yielding the desired sensitivity.

In FY 2013, all components for a 20-slab module will be brought together and tested. The limiting factor is cost per channel of digitizer. Nanosecond scale timing is critical for this application yet required significant spending in FY 2012. Some electronics design work will be necessary to scale up from the current 2-slab system. By early 2013, we expect to begin testing a 20-slab system with gamma and neutron sources, with later neutron beam testing that will mimic an environment closer to that of the final application. It is expected that algorithm work will advance throughout the year to improve the separation between neutrons and gamma-rays while increasing the efficiency.

Biological Sciences



Analysis of Functional Potential from Metagenome Data

Lee Ann McCue

In recent years, the technology to generate DNA sequence data has out-paced the development of analytical tools for these data. Novel computational methods to analyze the large quantity of sequence data being generated are needed, and will be essential for DNA-based studies designed to decipher the functional role of microbial communities in the environment.

Microbes exist and function in communities – studies of natural environmental or human-associated sites – often revealing hundreds to thousands of co-existing microbial species. Interactions between microbes in a community are complex, as is the impact the community as a whole has on its environment. Thus, deciphering microbial community activities in their natural environments is a prerequisite to understanding their functional role in environmental processes.

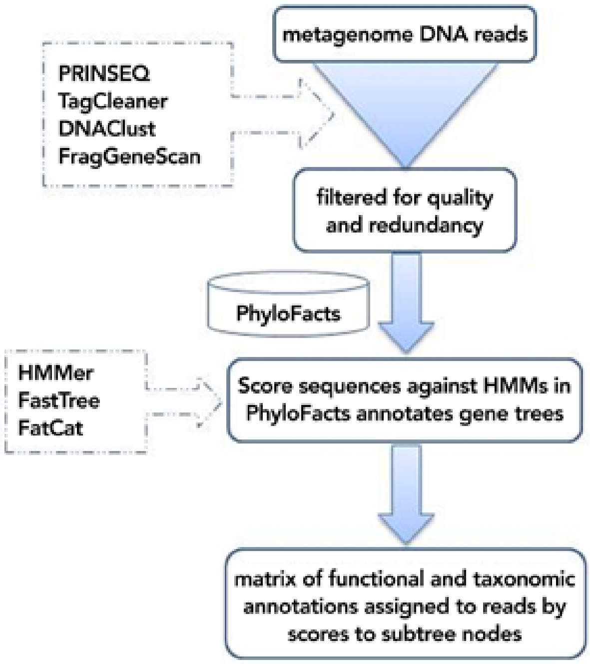
Studies of natural microbial communities have increasingly taken advantage of the advanced technologies now available to sequence DNA in a high-throughput manner. It is now feasible to sequence the DNA extracted from natural microbial communities consisting of many species. Such DNA samples consist of a composite mixture of genomes from all the community members (i.e., a metagenome). While some progress has been made using metagenomic data to infer the presence and abundance of microbial taxonomic groups, inferring their functional contribution to the community has proven challenging.

This research will develop a computational analysis approach for analyzing individual (unassembled) DNA sequence reads generated by current high-throughput sequencing technologies to provide information on the taxonomic composition *and* functional potential of the DNA source. This approach will utilize several established computational tools, combined with a database and novel software developed by our collaborator, Dr. Kimmen Sjölander. The advantage of this approach will be its ability to provide functional and broad-level taxonomic information for a much greater fraction of the metagenome than is currently possible using existing computational methods.

This project has been active for 5 months, during which time we have focused on identifying and installing on local computer systems the necessary tools for standard processes in our analysis (e.g., filtering DNA sequence reads for quality). In addition, we are porting the PhyloFacts database of annotated gene families to our computer system, and have identified an additional source of gene function information that will enhance the annotations currently in PhyloFacts. Specifically, we are designing a computer script to associate the functional annotations of genes contained in the SEED database with those in the PhyloFacts database.

In addition, we have identified a dataset on which we will test the approach. Illumina sequence data consisting of approximately 8 million sequence reads for a defined mixture of genomic DNA from 22 microbes are available. We are expanding the PhyloFacts database to ensure that the species of interest present in our test data are represented in the database, and in so doing, identifying methods and infrastructure that we will need to continue to expand the PhyloFacts database so that there is a broad representation of species. This will be key to ensuring the utility of our approach in the analysis of microbial community sequence data from diverse environments.

In FY 2013, we will finish porting and expanding the PhyloFacts database on PNNL computing systems as well as installing additional software tools needed for the analysis pipeline. Moreover, a significant effort will be committed to determining the sensitivity and specificity of the approach for predicting the taxonomic and functional composition of the test data set using this approach.



Flowchart of the computational analysis approach for metagenome data. Existing software tools being incorporated are shown in the hashed boxes.

PN12008/2409

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

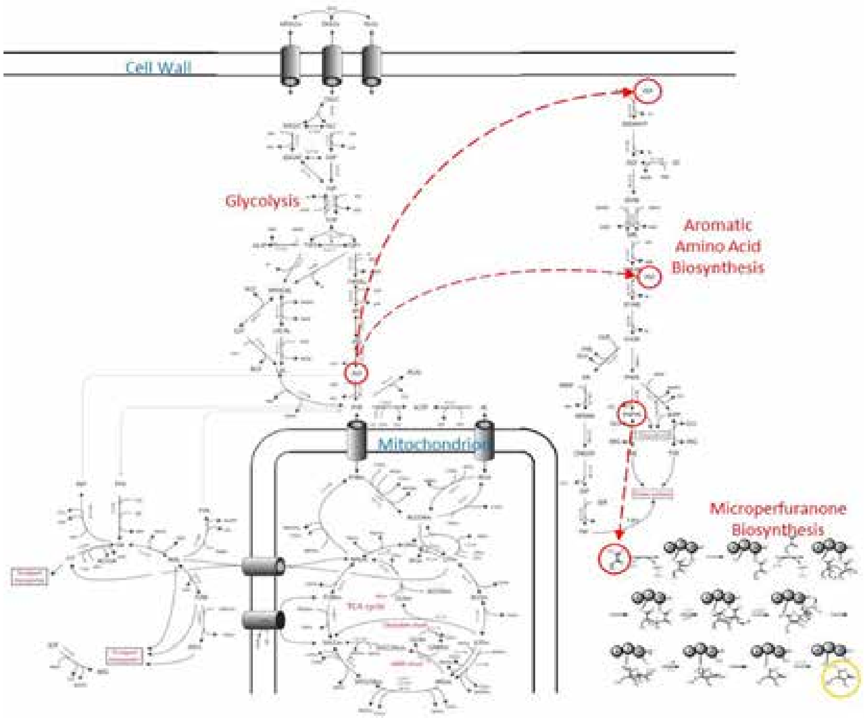
Kenneth S. Bruno

This project is developing new tools that will provide the means to discover 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 are secondary metabolite compounds whose natural material has been produced for decades in antibiotics and as therapeutic agents. Through genomics and advances in molecular biology, high levels of secondary metabolite production have been sought as a source of advanced biofuel. Like isoprenoids, polyketides have 10 to 50 carbon atoms that vary in degree of oxygenation (hydroxyl and ketone groups) saturation and cyclization. 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.

In FY 2011, we successfully generated strains that express metabolite genes from other fungi. We demonstrated that this single gene can generate the compound microperfuranone (mpf). In addition, we successfully developed and tested a means to perform metabolite analyses using gas chromotagraphy, as 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 for the first year of the project. This approach can greatly accelerate the throughput in and allow for the rapid screening of transformants.



Advanced biofuels metabolic production process using the cell as the production plant.

In FY 2012, we successfully generated more strains that can produce biofuel compounds. Compounds known as highly reduced polyketides hold promise as new hydrocarbon biofuels because of their lower oxygen content. We have taken highly reducing polyketide synthase (hrPKS) genes from other filamentous fungi and placed them into our production system. These compounds are derived from common metabolic building blocks such as Acetyl CoA. Understand-

PN11008/2330

ing how our system may be improved to produce higher amounts of these precursors is important in implementing technology that will increase production capacity. We also advanced metabolic modeling capabilities for a detailed mass balance approach to production tied to enzymatic function. This approach will allow predicting genetic changes to increase production.

In our approach, we used the production of a small mpf molecule. Using our host chassis system, we generated a strain containing the mica gene from *A. nidulans*. This gene codes for a synthase that can generate the mpf compound from substrates that are part of the normal metabolism. We took a previously established metabolic model for *A. niger* and translated into the COBRA toolbox to for production of mpf to generate a map of each enzymatic reaction involved in converting glucose, our substrate. Experiments were conducted where mpf was generated under conditions in which *A. niger* overproduces citric acid. Data indicate that production of mpf can occur in parallel with production of small organic acids. Further application of the model may help us choose genes that can be up or down regulated to shift the mass flow from one product to another.

During the last fiscal year, we also tested SPME for higher throughput analysis to support rapid screening. This method was used to test for the production of volatile compounds by our system. These tools are an invaluable resource for expanding the utility of our biofuel production chassis.

Automated Thermal Image Processing to Identify and Enumerate Targets of Interest

Corey A. Duberstein

Our objective was to explore automatic methods to differentiate birds and bats from other observed phenomena captured on digital infrared video.

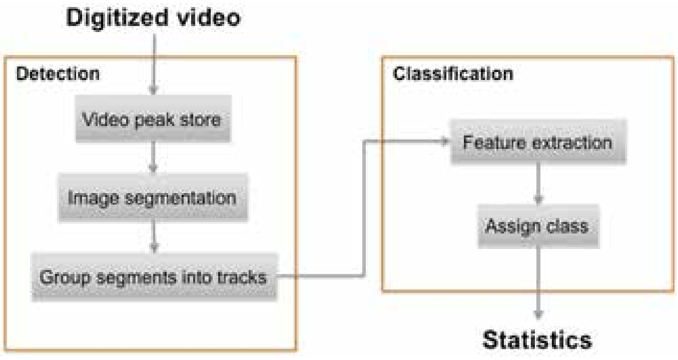
Previous research indicated that the use of infrared video cameras was an effective method to survey the sky for birds and bats. Unlike traditional methods that require a human observer recording events as they are observed, video recording provides a real-time archive of what was observed and could be conducted at remote locations. However, the identification of observed phenomena still requires a trained observer viewing the video, which becomes both time consuming and expensive and, like traditional methods, is still prone to observer bias. The wind energy community expressed the desire for a tool that would standardize methods for and reduce cost of assessing wildlife populations in a semi-remote setting. Automated processing and classification of birds and bats recorded on infrared video would enable remote assessment of wildlife populations potentially impacted from wind energy development, enable informed decision-making in a timely manner, and thereby lower the environmental impact and cost of alternative energy development.

The outcome of our research is software that would allow for the rapid processing of infrared video by converting digital video into numerical information. To accomplish this, we devised methods to condense recorded video and identify thermal tracks of observed phenomena from an existing infrared video library. The effectiveness and robustness of thermal track identification methods and data extraction techniques were statistically evaluated.

A new algorithm for automatically detecting birds and bats in infrared video was designed and implemented in Matlab. The algorithm was developed using a dataset provided by Dr. Sid Gauthreaux of Clemson University. The algorithm design is a unique combination of video peak store (VPS) processing, region growing, and perceptual grouping techniques. Birds, bats, and other warm targets moving through the camera's field of view (FOV) produce bright spots in the video that change position from frame to frame. VPS is the process of storing the peak intensity of each pixel in the video over the course of a fixed time window into a single image. The resulting image then contains the history of a target's motion, or its track, through the camera's FOV.

VPS is usually accomplished with a dedicated hardware device, but we wrote our own software to perform the VPS processing. The algorithm then detects tracks in the set of VPS images produced from a video recording. Conceptually, a track is composed of a series of objects. An object is a spatially connected group of pixels that had peak values in the same frame. Individual pixels are first grouped into objects using a form of region growing that was tailored to this application. Objects are then combined into tracks using perceptual grouping, a general method of image processing inspired by human visual perception. In our algorithm, similar objects that lie in a line or along a curve are grouped together as a track. The bulk of the algorithm development work was defining "similar" and "lie in a line or along a curve" in an appropriate mathematical form.

Tracks are reported in a text file for import into various software formats for further analysis. Each track is identified by the time it starts in the recorded video for independent verification with observer annotations. The text file also contains a number of measures of each track, such as the mean size and intensity of the objects in the track, and the sinuosity of the track. The sinuosity is a measure of the change in direction between successive objects in a track. Preliminary testing showed that the algorithm detected 96% of the tracks of flying birds and bats visible in the video.



Conversion of digital infrared video into tabular attributes and then classified into functional groups (i.e., sea bird, songbird, bat, insect) based on thermal track characteristics.

PN12010/2411

Characterization of Signaling Networks in Single Cells

Bryan E. Linggi

Our experiments characterize signaling networks in single cells using microfluidic systems to decrease sample input and increase molecular measurement resolution. Characterization and enumeration of signaling network variability "states" will greatly advance our understanding of cellular responses and community behavior.

Cell communities exhibit complex responses to changes in their environment. Studying associated molecular changes (e.g., RNA and protein) is likely to improve predicting the behavior of these communities and engineer them for human benefit. However, traditional assays that measure changes at the population level obscure the underlying cell-to-cell variability that exist even in the homogenous population. By understanding differences in signaling at the cell (rather than population) level, we can begin to unravel the apparent heterogeneity in cell response (so called "rare-events") that mediate many biological processes. However, 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 occurring at the phenotypic (i.e., cell response) level. Thus, there is a critical need to measure molecular changes at the single cell level to understand the inherent variability among cells and appropriately link them to cellular behavior.

In FY 2011, we optimized multiple approaches to capture and analyze single cells using microscopy and microfluidic devices. We also created several microfluidic designs to capture cells, which were typsinized, loaded into devices, and captured using a variety of different "capture wall" geometries. Additionally, we designed devices that allowed for precise control of two-fluid interfaces, increasing the throughput of the system. Finally, we created four different clonal populations (single cell derived) cell lines for future use and allowed for dual color imaging for quantitating cell cycle and transcription factor activity in a single cell.

For FY 2012, we performed extensive analysis of all critical aspects of culturing cells in microfluidics devices for single cell RNA quantitation. We developed devices using multiple capture strategies, effectively delivered cells, and created prototype devices that enabled gradients of buffers to enable spatially precise lysis of single cells among an arrayed cell group. We also successfully identified critical parameters for cell attachment by investigating the influence of typsinization time and concentration, media type and supplements, and cell density. As a result, we made three findings: 1) cell density was critical in this experiment; 2) we could achieve only a ~30% survival of attaching cell in the device when low numbers (~30 cells) are delivered due to the requirements of downstream analysis; 3) this low viability is a feature of even robust cells such as Hela.

Multiple next steps could overcome this limitation, such as increasing throughput for this decreased survival, which would allow for effects of dead or dying cells in the local area of analyzed cells. This situation could be a critical difference between cell RNA levels. Parallelization of the device would allow selection of optimal groups of cells. Considering these results and the timeline and resources for this project, we switched efforts from RNA analysis in single cells and instead pursue a promising development for analysis of single cell phenotype. Thus, our revised aims are noted below.

Develop cell micropatterning techniques to constrain cell geometry and microenvironment. We optimized a procedure for patterning cells using a negative PDMS mold that allows patterns within a precision of ~2 µm of hydrophilic patterns to attach any hydrophilic substrate, such as laminin or fibronectin, in which cells can bind. The remainder of the plate in which cells cannot bind is coated with a hydrophobic solution of pluronic acid. We created patterns of 20, 30, 40 and 50 µm diameter circles with a space of 50 µm from center to center. These sizes and distances are easily customizable.

Create cell lines for phenotype analysis of S-phase entry. We additionally created high expressing clones cell lines that express the cell cycle reporter FUCCI. This is a fluorescent reporter that allows live cell identification of cells that enter S-phase. To identify all cells (not just S-phase), cells were generated to express a GFP protein. Finally, dual FUCCI/GFP cells were enriched for high expressors using flow cytometry.

Identify influence of microenvironment on S-phase entry. We are now positioned to begin experiments using these cells grown on micropatterns. There are many variables that can be precisely modulated using these cell and soluble stimulators or inhibitors of cell adhesion, including laminin and E-cadherin. These experiments should yield valuable data concerning how cells are modulated by these interactions and how it ultimately affects S-phase entry.

In FY 2013, we will characterize efficiency and optimize cell micropatterning, identify differences in cell response in single versus multiple cells, and determine mechanisms for differential responses due to cell density. From this work, we anticipate submitting at least two publications.

PN11011/2333

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

Susan D. Wiedner

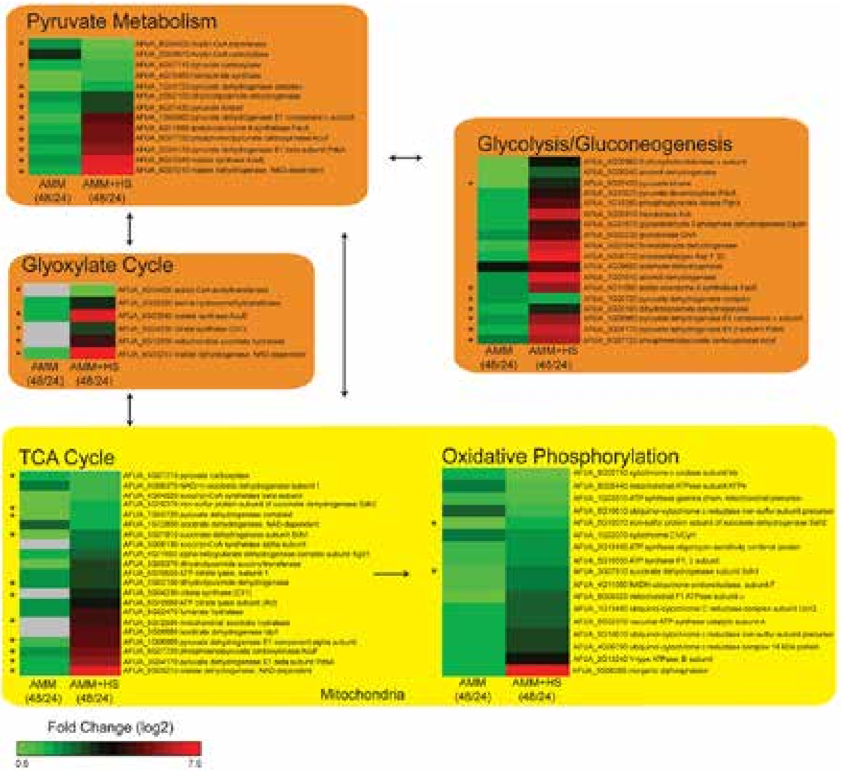
We seek to combine the proteomic technologies of activity-based protein profiling (ABPP) and subcellular proteomics. Individually, these two technologies study different "fractions" of the proteome and in combination would provide spatiotemporal information of the functionally active proteome.

ABPP and organellar proteomics are techniques used in proteomics to decrease the complexity of the natural cellular proteome, which often contains thousands of proteins. Specifically, ABPP isolates the active portion of the proteome by tagging functionally active enzymes with chemical activity based probes. In 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. On a cellular level, this information would help elucidate 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 2011 included studying *A. fumigatus* with ABPS using liquid chromatography-mass spectrometry (LC-MS). Global cell lysates of *A. fumigatus* and non-pathogenic related fungi *Neosartorya fischeri* and *A. clavatus* grown in the presence or absence of human serum were treated with a novel general cysteine reactive activity-based probe and a new serine hydrolase specific probe. Sample preparation, LC-MS analysis, and bioinformatics data analysis were used to identify the tagged enzymes. The active proteome of the three aspergilli were compared.

During FY 2012, 48 datasets spanning two culture conditions (HS or no HS), two time points (24 h or 48 h), and three aspergilli were analyzed. We found that human



Differences in enzyme reactivity of A. fumiatus over time, dependent on culture condition. KEGG pathway = All proteins with [fc]>2 were mapped onto KEGG glycolysis/gluconeogenesis, TC cycle, pyruvate metabolism, glyoxylate cycle, and oxidative phosphorylation pathways; yellow = processes occurring in the mitochondria; orange = processes in cytosol; arrows = pathway products are used in other pathways; heat maps within each pathway = fold change of 0.5 to 7.5 (log2 scale) calculated for enzyme reactivity over time for each condition (i.e., AMM+HS_24 h vs. AMM+HS_48 h and AMM_24 H vs. AMM_48 h); grey boxes = proteins that did not make a 10% protein coverage cut-off; * = protein maps to more than one KEGG pathway.

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serum greatly altered protein reactivity, and that protein reactivity within HS culture was different between the closely related fungi. Further, protein reactivity was different over time in the presence or absence of HS; HS induced increased reactivity of metabolic (including fermentation) and energy processes. Our data suggests functions in *A. fumigatus* but not the other fungi that may be contributing to infection, such as lipid signaling pathways. This analysis resulted in a high level publication describing functional activity of *A. fumigatus* and another describing the comparison of the three fungi is being prepared. The analysis of the proteome of the pathogen will facilitate analysis of the host proteome in an infection model and will increase the chance of identifying pathogenic proteins or biomarkers in a host infection model.

During FY 2013, we will shift our focus from the study of *A. fumigatus* to the study of host-pathogen interactions. The lysosome and acidic organelles play a key role in microbial defense by macromolecule and protein degradation; *A. fumigatus* is able to evade cellular defense by residing in acidic organelles where it can then germinate and escape leading to infection. We will develop new ABPs that specifically target acidic organelles. Our new probes will incorporate an acidotropic weak amine to target lysosomes and endosomes, an alkyne moiety for incorporation of either an affinity enrichment handle (biotin) for LC-MS analysis or a fluorophore (rhodamine) for in-gel analysis, and a general cysteine protease warhead to facilitate enzyme class coverage in order to optimize the discovery of unknown enzymes. In addition, we will investigate intact in cell labeling for optical imaging. By tagging and enriching acidic organelle reactive proteins we are effectively reducing the complexity of the proteome by activity-based and organellar enrichment. This technology will allow monitoring of reactive proteins over time and disease progression (STEAP) using a variety of techniques. We will then implement our new STEAP pathway on an epithelial cell infection model (A549) to investigate changes in host enzyme activity induced by the uptake of *A. fumigatus* conidia.

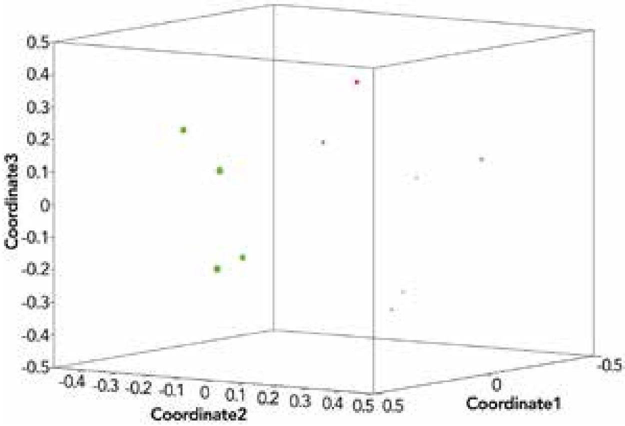
Community Diversity and Functional Redundancy of Cellulytic Microbial Communities in Soil Aggregates

Vanessa L. Bailey

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 less than 1000 µm in diameter. In prior project years, we focused on the metabolism of cellulose, earth's most abundant natural biopolymer, and developed a highly sensitive fluorescence-based cellulase (β-glucosidase) enzyme assay to reveal the functional capability and resiliency of the community to perturbation. We also developed DNA isolation techniques that produced sufficient high-quality DNA for pyrosequencing of the 16S ribosomal RNA gene from individual aggregates.



Non-metric multidimensional scaling ordination of the community structures of high (green) and low (red) activity samples; symbols are scaled to reflect the abundance of the significantly differentially represented (q < 1e-06) member of the family *Chitinophagaceae*.

Microscale enzyme assays measuring β-glucosidase activity of individual aggregates 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. Our analysis of the microbial communities present in individual soil aggregates revealed that the species richness of an aggregate was thoroughly sampled with only a few hundred 16S sequences. Analysis of the β-diversity of the aggregates showed that each aggregate had a relatively unique community dominated by only a few different microbial types, with these dominant microbes varying between aggregates.

Integrating these approaches, we performed these assays in tandem during FY 2012, determining the β-glucosidase activity of aggregates and examining the microbial community by 16S pyrosequencing. The richness and diversity of the microbial communities associated with high β-glucosidase activities were not significantly different from those of the low β-glucosidase activity communities; however, analyses of variance clearly show that the communities of these two groups differ. The separation of groups is partially driven by differential abundances of members of the *Chitinophagaceae* family. Interestingly, this separation is based on differential abundances, suggesting that either closely related strains not differentiable via 16S sequencing are functionally different or the presence of appropriate substrates in the high activity aggregates enhances the abundance and activity of key organisms that may be present but not stimulated in the low activity aggregates.

This research has developed new approaches to link community phylogenetic composition with functional potential. As we demonstrated that this link in soil communities is capable of cellulose degradation, this finding will advance our fundamental understanding of the global carbon cycle in the terrestrial biosphere and partly fulfill the DOE mission to address energy and environmental challenges associated with CO_2 emissions.

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

Matthew J. Marshall

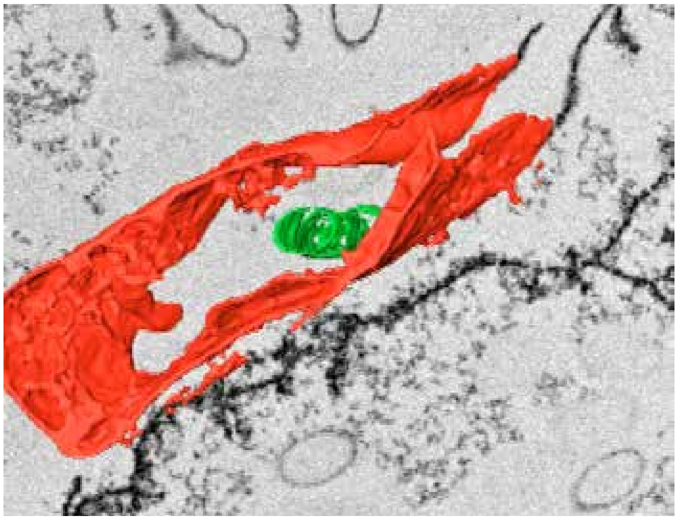
This research develops correlated capabilities for state-of-science imaging, compositional analysis, and functional characterization of microbial biofilms and seeks to understand biofilm influences on biogeochemical processes such as the fate and transport of radionuclides in the subsurface or carbon 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 3D 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 (μXRF), scanning transmission x-ray microscopy (STXM), and nano-secondary ion mass spectroscopy (nanoSIMS) to produce high-sensitivity, element-specific distributions which correspond to electron microscopy images and 3D 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 were 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 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 to understanding nm-scale interactions of UO_2 with EPS involved the serial sectioning and 3D reconstruction of cells and the EPS matrix associated with UO_2. Reconstructions of *Shewanella* cells and the UO_2-EPS matrix are in progress.

In FY 2012, we began generating highly reproducible biofilms for imaging studies and chemical analysis, *Shewanella* cultures were grown using anaerobic minimal medium containing lactate and fumarate in a constant-depth (bio)film fermenter (CDFF) to a thickness of ~200 μm on 5-mm-diameter plastic (GelBond™) substrates. This substrate is amiable to thin sectioning and facilitates high-resolution, depth-resolved biofilm morphology studies using EM. Unfortunately, the amount of chemical information that can be collected during EM analysis is limited and complicated by



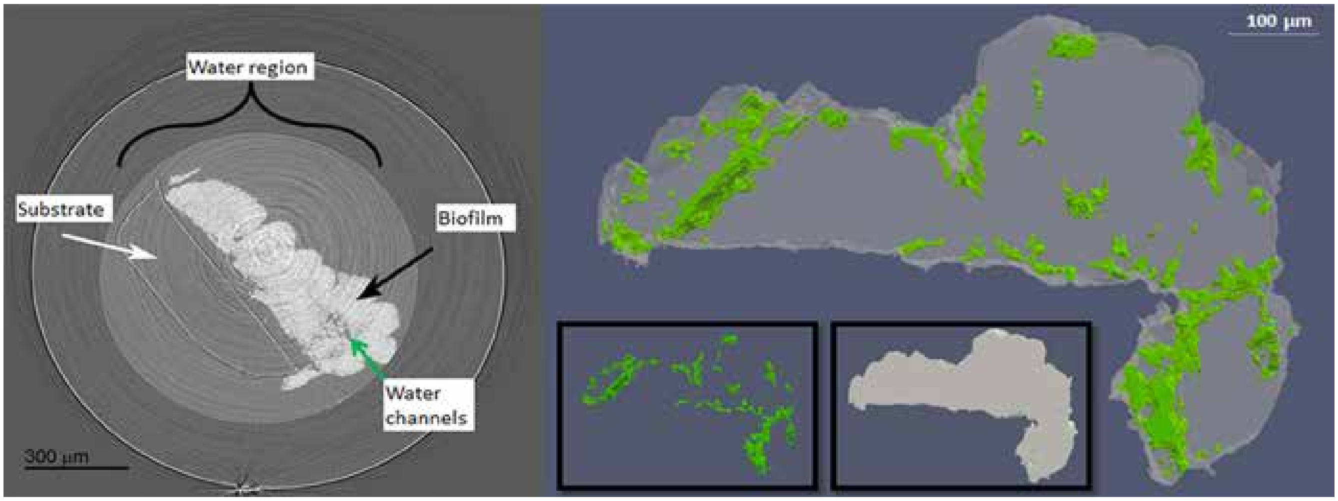
Amira 3D reconstruction of Shewanella cell and EPS matrix associated with UO_2. The cell can be seen in close proximity with UO_2-EPS.

the addition of chemicals for EM fixation, dehydration, staining, and embedding.

Correlative soft x-ray-based imaging techniques present an excellent opportunity to gain chemical and/or elemental information from ultrathin biofilm sections at relevant spatial resolutions. A limitation to obtaining high-quality data is the addition of traditional sample processing chemicals such as aldehydes that interfere with carbon edge spectra during STXM or produce interfering infrared signatures. We developed a new cryosample preparation technique that omits traditional sample processing chemicals that produce data interference. EM analysis confirmed that excellent depth-resolved biofilm morphology and cell ultrastructures were well preserved. Samples were then imaged by STXM, µXRF, or nanoSIMS to obtain nm-scale chemical information that could be correlated to high resolution EM images. We investigated carbon chemistry using STXM and found several differences between the cell surface and EPS matrix-encompassing biofilm cells. This high-resolution visualization of biofilm chemistry at the nm scale will help determine how biofilms influence local biogeochemical reactions.

For pore- and/or community-scale investigations, a variety of surface imaging tools (i.e., secondary electrons or helium ions) are available. However, understanding biofilm structure in complex 3D environments such as a soil particle is considerably more difficult. X-ray microtomography can provide 3D 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 makes detecting biofilms difficult. Phase contrast imaging can provide enhanced contrast of low-Z materials and some methods provide texture-based contrast modes as well. During FY 2012 x-ray experiments, we used three physically distinct signatures—absorption, phase, and scatter—for imaging biofilms on complex matrixes. Biofilms grown in the CDFF or on the surface of a hollow fiber were examined using high resolution x-ray microtomography (0.74 µm/pixel sampling) and with a Talbot interferometer (2.00 µm period fringe pattern). In these studies, biofilm samples were imaged dehydrated or in a fully hydrated form. To distinguish biological material against higher-Z substrates, an osmium contrasting agent (e.g., stain) was added to some samples to differentiate between organic materials and substrates. Preliminary 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. Our findings suggested that phase contrast enhances the visibility of unstained hydrated biofilms (relative to absorption contrast), while scatter provides little additional information on the hydrated samples. Using osmium as a contrast agent enhances visibility for absorption-based imaging. For relatively thin biofilms (~50 µm or less thick), spatial resolution loss from the use of a 2-µm fringe pattern must be weighed against the ability to image without a contrast agent.

Through collaboration with another project, 3D reconstructions and segmentation of reconstructed slices have visualized pores (or channels) in the hydrated biofilm. These pores indicate regions where water, nutrients, or electrolytes can flow through a biofilm and may influence pore-scale biogeochemical reactions such as contaminant fate and transport. For FY 2012, we significantly narrowed the technology gap between EM and x-ray capabilities. Our experiments have facilitated the initial construction of both micrometer and nm scale biofilm models. For FY 2013 experiments, we will extend this research and integrate the knowledge from both the micro- and nano-scale models into a single high-resolution, 3D chemical image of a biofilm community.



Left: Reconstruction of a single slice on an x-ray absorption microtomography experiment showing an osmium stained biofilm imaged in water at 13keV and 0.7 um/pixel resolution. The substrate and biofilm are visible in the water region (inside a pipette tip). Right: Segmentation of 50 reconstructed slices of biofilm (representing ~35 µm thick [z-direction]). Water channels have been selected and clearly illustrate interconnectivity of the channels throughout the biofilm. Internal structure suggests connectivity from outside of biofilm to bottom (i.e., surface attached face). Insets illustrate water channels in green and gross biofilm morphology in white.

PN11015/2337

Development of Functionalized Nanoporous Materials for Bioenergy and Biomedical Applications

Chenghong Lei

We are developing a transformational material platform that allows 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 immobilization. In general, low efficiency of conventional immobilization approaches is mainly from 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.

Our goals have focused on further developing functionalized mesoporous silicas (FMS) and other alternative nanomaterials (Nano Clay, Nano TiO_2, and graphene) 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 have been working to build a transformational technological platform to allow for high loading density of biomolecules with high efficiency of biomolecular activity based on functional nanostructured materials. Our progress during FY 2012 in the following tasks is detailed below.

Development of functional naomaterials. Besides working with FMS, we characterized uniquely prepared Nano Clay and Nano TiO_2 nanoparticles stabilized at neutral pH for super high protein loading density potentially for biomedical and energy applications. We also functionalized graphene and graphene oxide with mRNA and electron transfer mediators for biomedical applications.

Bioenergy and biomedical applications based on functional nanomaterials. We established fast and reliable *in situ* regeneration of NADH via lipoamide dehydrogenase (LD)-catalyzed electron transfer reaction to regenerate the bio electron donor characterized by spectroelectrochemical method. The NADH regeneration system was successfully coupled with lactate dehydrogenase for the enzymatic conversion of pyruvate to lactate. We have also explored the way to combine the *in situ* regeneration of NADH with formate dehydrogenase and alcohol dehydrogenase for conversion of carbon dioxide to useful compounds.

In collaboration with Dr. Thierry Boon in Brussels, Belgium, we obtained the best *in vivo* efficacy with FMS-loaded IL-22 (one cytokine) potentially for cancer immunotherapy. The test involves injection in the mouse ear and observation of inflammation by measuring the weight of the ear. We found that even under the heated condition, the nearly native conformation and activity of a protein can be hoarded in FMS via non-covalent interaction. Surprisingly, the protein released from the heated protein-nanoporous composite can still maintain its nearly native conformation and activity, while the free protein was permanently denatured under the same treatment.

Glucose oxidase (GOX) was spontaneously and largely entrapped in aminopropyl-functionalized mesoporous silica (NH_2-FMS) at 20°C via a dominant electrostatic interaction. We found that after the FMS-GOX composite was incubated at 60°C for 1 h, the released GOX from the thus heated FMS-GOX composite maintained 89% of its initial activity prior to the GOX entrapment, while the free GOX in solution lost nearly all activity under the same incubation. Native electrophoresis and intrinsic fluorescence emission of GOX demonstrated that the heating resulted in significant conformational changes and oligomeric aggregation of the free GOX, but FMS efficiently resisted the thermal denaturation and oligomeric aggregation and accordingly maintained the nearly native conformation of GOX therein. Our results demonstrate that FMS can hoard the protein in a nearly native conformation via non-covalent interaction even at a higher temperature than that inside or outside.

Finally, we obtained super high protein loading density of butyrylcholinesterase against organophosphate nerve agents, immunoglobulin G (IgG) for cancer immunotherapy, and other proteins on our uniquely prepared nanoclay and nanoTiO_2. We observed the slow release of these protein drugs under physiological conditions. We also functionalized the graphene oxide with mRNA probes and successfully delivered the probes into living cells. The probes show a good response for their targets. The results indicate that graphene oxide nano sheets are excellent nano-platform for gene delivery and for in vivo cell imaging. Graphene nanosheets were also functionalized with an electron transfer mediator, Prussian blue nanocubes, and enzymes for fabrication of a sensitive biosensor for detecting organophosphorus agents.

PN11026/2348

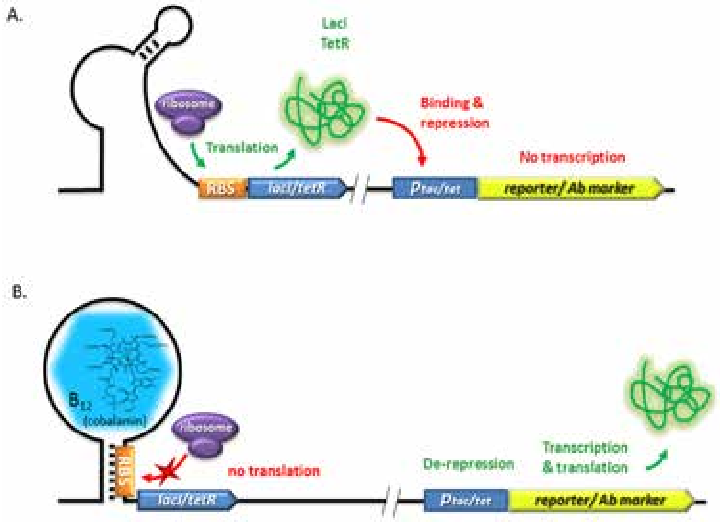
Directed Strain Evolution through Riboswitch-Controlled Regulatory Circuit

Alex S. Beliaev

The project explores state-of-the-art metabolic engineering approaches for scalable and cost-efficient production of biofuels and bioproducts. This is accomplished through development of new synthetic biology tools that will drastically accelerate the process of metabolic engineering using principles of directed evolution.

Current metabolic engineering strategies involve modification of specific targets (reactions, pathways), that lead to significant improvements in product yield and productivity. As this approach requires clear understanding of the organism's genetic and metabolic makeup, its success is often confounded by unanticipated regulatory features, feedbacks, or interactions. In contrast to direct engineering, strain evolution does not require *a priori* knowledge of the system and takes advantage of genetic diversity and evolutionary forces. With few exceptions, however, the selective pressure can rarely enhance product yields, as natural selection forces will target the functions essential for survival.

We propose to address this issue by using riboswitch-controlled synthetic circuits that transform cellular input into a signal that triggers expression of growth-essential function. By placing genes essential for survival under the control of these regulatory circuits and applying selective pressure, the system will yield strains that have evolved to overproduce the riboswitch-specific metabolite. The proof-of-principle work proposed herein will exploit the applicability of riboswitch-controlled circuits for directed strain evolution and product yield optimization. The expected outcomes of this project include 1) engineering of synthetic regulatory circuits; 2) developing approaches and toolkits for directed strain evolution; and 3) conceptual developing of metabolic engineering and synthetic biology strategies to apply to the design of novel platforms for cost-effective biofuel production processes.



Development of riboswitch-controlled cobalamine-dependent synthetic regulatory circuit. (A) In the absence of cobalamine, the LacI or TetR protein shuts down gene expression by binding to tac or tetO promoter. (B) When cobalamine is present, the sequestration of ribosome binding site (RBS) blocks the translation of LacI/TetR subsequently derepressesing the tac- or tetO-driven gene expression.

Despite a mid-year start, the project has made significant strides towards developing synthetic regulatory modules that can modulate gene expression in a ligand-dependent manner. For the proof-of-principle demonstration, we selected the naturally occurring riboswitch of *Shewanella oneidensis MR-1* involved in cobalamin (vitamin B_{12}) biosynthesis and used it to build a set of synthetic transcriptional repressor molecules (LacI or TetR) whose 5-foot untranslated region contained the riboswitch sequence. These constructs were subsequently incorporated into our synthetic two-component circuit to control the expression of reporter (GFP, YFP) or antibiotic marker (kanamycin or gentamycin) cassettes in a ligand-dependent manner. The latter is achieved through translational attenuation of LacI and TetR by cobalamine, which positively affects the expression of the output module (reporter or antibiotic markers). We have also modified the phenotype of the host organsm (i.e., *S. oneidensis MR-1*) to start testing the dynamics of the constructed circuit function and evaluating its performance based on the response curve quantitatively linking ligand (cobalamin) concentration and protein levels. The synthetic riboswitch-controlled circuit will be modified as necessary to display a broad dynamic range, low background response levels, and specific sensitivity integrated into *S. oneidensis MR-1*. The ability of the riboswitch to confer antibiotic resistance only in the presence of cobalamin will be used to drive the evolution process toward strains displaying (significantly) elevated levels of vitamin B12 biosynthesis.

If we are successful in demonstrating the utility of synthetic riboswitches for directed strain evolution, we propose to initiate the development of synthetic regulatory circuits for detection specific metabolites. These should include efforts that will utilize and strengthen PNNL expertise in computational biology, molecular modeling, and combinatorial chemistry. The range of applications involving synthetic riboswitch-based regulatory circuits include biofuels production, biological monitoring, and national security.

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

Thomas C. Squier

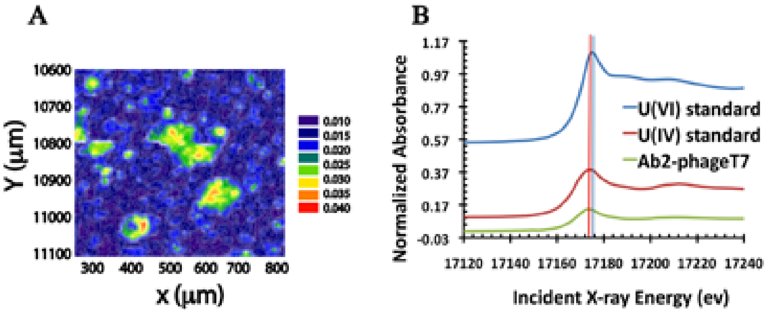
We propose a multidisciplinary collaboration to study systematically the bacteriophage-bacterial interactions in the uranium subsurface contaminated Rifle Integrated Field Research Challenge (IFRC) and use this information to enhance U(VI) bioremediation.

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).

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 and found the best candidate for further phage in UraR from *Gluconacetobacter hansenii* ATCC 23769. We solved the x-ray crystal structure of UraR and submitted the coordinates to the PDB database (file 3S2Y). We successfully established three randomized mutation pool screening for chromate/uranium reduction and found that several small peptides derived from these pools showed promising chromate reduction. Finally, we 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 can reduce U(VI) to U(IV) at the phage surface.

In FY 2012, we created phage-library containing cDNA from bacteria strains *Geobacter sulfurreducens*, *G. riflensis* (M21), and *Shewanella oneidenesis* (MR-1), primarily screening the first and final strains. High-throughput screening of pools of recombinant phage mutations for chromate reduction, coupled uranium absorption, and uranyl reduction measurements have identified several bacteriophage mutants capable of chromate and uranium bioremediation. The peptide sequence anlysis suggested these peptides may reduce uranium similarly like the amyloid peptide (Aβ) aggrigation in human brain (*Applied and Environmental Microbiology* manuscript). Alzheimer's disease is associated with the abnormal aggregation of amyloid-beta (Ap) protein. Ap and its precursor protein interact with metal ions such as zinc, copper and iron. It is possible that one electron is donated from each subunit of Aβ, electron donation from Aβ creates a putative radical (Aβ:Aβ+•) in a metal ion dependent manner. Our studies found the recombinant phage bearing the catalytic polypeptide showed significant potential for chromate and uranium reduction.



XANES analysis U(IV) presented on the T7-Aβ phage samples. A. The uranium map from the mount section samples collected after incubation of purified T7-Aβ phage with uranium (VI). B. The integration and comparison of T7-Aβ phage samples (red) to standards: uranyl nitrate (blue) and UO_2 (red), suggested U valence state of uranium (IV) presented on the surface of T7-phage bearing Aβ peptide.

PN11033/2355

Higher-Throughput, More Sensitive Stable Isotope Probing

Helen W. Kreuzer

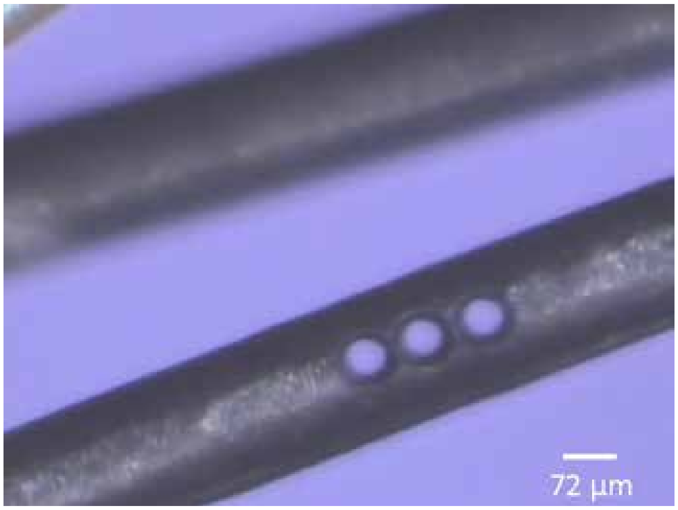
This project develops sensitive, higher-throughput stable isotope probing technology, including more sensitive instrumentation for measuring isotope ratios and methods for targeting specific microbes in a mixed population.

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

- identifying 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
- developing 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. 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.

Technology development. One part of this project 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 (LA-C-IRMS) method to be described in the literature, reducing the sample size required for analysis by nearly 1,000-fold (see figure). A paper describing this system was published in *Rapid Communications in Mass Spectrometry* and attracted national attention as highlighted in several media outlets, including ScienceNOW and Wired. We received additional funding from an external client to modify the instrument for measuring O isotopes and were invited to collaborate on two fish ecology research proposals, both of which have been funded. This instrument is also being used to analyze C metabolism in natural microbial mats as part of an ongoing DOE-funded research project.



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

In addition to the LA-C-IRMS system, we developed a capillary absorption spectrometer (CAS) for measuring the isotopic content of CO_2. This device is the most sensitive instrument ever developed for measuring the stable isotopic content of CO_2 and offers the potential for analyzing the C from a few microbial cells. A manuscript describing this system was published in *Reviews of Scientific Instruments*, where it was noted as a research highlight. Further, we showed that the CAS could be coupled to a laser ablation unit and measurements made in flow-through mode, another key technological innovation.

This technology was deemed so promising that it received funding from the Environmental Molecular Sciences Laboratory (EMSL) via a partner proposal, in which CETAC (a manufacturer of laser ablation systems) and Opto-Knowledge Systems Inc. (OKSI-a manufacturer of capillary optical waveguides) donated parts and staff labor. EMSL invested in a

PN09036/2204

state-of-the-art G2 excimer laser ablation system from Photon Machines with size resolution down to 2 µ. Coupled with the CAS system still under development, this will allow isotopic imaging of carbon, oxygen and nitrogen at the level of 2 µ. This LA-CAS imaging system will be part of an EMSL capability available for routine use by the scientific community.

Targeting specific microbes. Our strategy for analyzing specific microbes within a microbial community was to isolate RNA molecules from those organisms using approaches based on their unique base sequences and analyze these molecules as proxies for the organisms. We developed two approaches for accomplishing this goal: the first uses oligonucleotide probes linked to magnetic beads selectively to capture specific RNA molecules from a mixture. While this method had previously been described, we conducted systematic studies to increase yield and specificity and successfully captured RNA of a target organism from a complex mixture. Pioneered by a team member, the second approach uses sequence-specific deoxyribonucleozymes (DNAzymes) to cut RNA selectively from the organism(s) of interest, which generates fragments that can be separated from the population because of their small size. We used capillary electrophoresis and high performance liquid chromatography to achieve this separation.

Whether the target RNA is captured by magnetic bead hybridization or by specific cutting, it is recovered in a solution and typically in small amounts. We therefore constructed an interface for measuring C isotope ratios in dissolved solutes (such as RNA) or suspended particles (such as cells) from aqueous solutions. The interface has a theoretical sensitivity of 10 ng C, approximately 1,000× more sensitive than standard technology. We interfaced this device with the isotope ratio mass spectrometer and made isotope ratio measurements, and the instrument is ready for use.

Future directions. The technologies and methods developed under this project have been incorporated into several ongoing projects. The laser ablation-capillary absorption spectrometer is undergoing further development and promises to provide a unique ultra-sensitive, rapid method for spatially resolved isotopic analysis at the scale of individual or a few cells. This capability will be made available to the scientific community via the EMSL.

The laser ablation-combustion-isotope ratio mass spectrometry system has garnered funding from diverse sources. Our team was approached and funded by the North Pacific Research Board about a project collaboration on testing the use of the LA-C-IRMS in retrospective studies of marine productivity in the North Pacific to understand what led to a crash in the herring population there. In addition, we received U.S. State Department funding to modify the laser ablation-combustion-isotope ratio mass spectrometer instrument for O isotope ratio measurements. In turn, this led to another proposal (now funded) to Idaho Power and Light to determine whether spatially specific measurements of O isotope ratios in fish otoliths could be used to track the thermal history of migrating salmon, which will lead to more efficient water management in the Columbia and Snake River basins.

Additionally, the project team has been incorporated into another large-scale microbial ecology project. PNNL has a long-term research program funded by DOE’s Office of Biological and Environmental Research that focuses on interactions between microbes in natural and model communities. The project lead was invited to bring isotopic approaches to the project and was made an internal co-principal investigator, and another team member was named a key contributor. Together, we will apply techniques developed under this project toward the goal of understanding how members of these communities interact to carry out biogeochemical cycles that sustain all life.

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

Aaron T. Wright

This project develops a sensitive, broadly applicable chemical proteomics technology–multiplexed activity-based protein profiling–for characterizing functional enzyme activities from myriad organisms. Applying this method improves our 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. In this approach, chemical probes are applied to complex biological systems to directly report on the functional activity of enzymes within native physiological settings. To realize the rapid, sensitive individual measurement of multiple enzymes from unrelated families simultaneously in native samples, we transformed this technology into a quantitative, multiplexed *in situ* approach.

In FY 2012, we demonstrated that our multiplexed activity-based protein profiling (MABPP) mass spectrometry-based proteomic approach is capable of contributing to widely different biological systems. We applied technology to provide functional annotation and gain a greater understanding of key enzymatic functions in the lung pathogens *Mycobacterium tuberculosis (Mtb)* (bacterial) and *Aspergillus fumigatus* (fungal). We developed novel chemical probes to identify protein targets, including cytochrome P450 enzymes, of antifungal agents in *Mtb* and *A. fumigatus*. In a biofuel project, we applied a multiplexed probe approach to identify the complementary suite of hydrolytic enzymes that facilitate lignocellulose degradation in the fungus *Trichoderma reesei*.

In addition to important biological research findings, we developed novel, improved, technical, and data analysis features of activity-based protein profiling, including 1) a large chemical probe suite to profile broadly numerous enzyme functions in prokaryotic and eukaryotic organisms; 2) quantitative data analysis methods, including accurate mass and time tag MABPP (AMT-ABPP); 3) aligned proteogenomics and hidden Markov modeling with MABPP for improved functional annotation of organisms; and 4) improved sample preparation techniques and data normalization for improved data quality.

We made significant progress toward understanding the functional proteolytic enzymes in *Mtb* that contribute to the organism's viability and host invasion, persistence, and pathogenesis. We annotated its adenosine proteins, revealing widespread novel nucleotide binding function. It is well known that the computational prediction of protein function is often error-prone and incomplete. In *Mtb*, ~25% of all genes have no predicted function and are annotated as hypothetical proteins, severely limiting the understanding of *Mtb* pathogenicity. We employed MABPP to probe, annotate, and validate nucleotide-binding proteins in *Mtb* that experimentally validated prior *in silico* predictions of > 250 proteins and identified 73 hypothetical proteins as novel nucleotide binders and chose proteins with diverse unrelated sequences for an expanded view of adenosine nucleotide binding. Further, several nucleotide probe binders are essential or taxonomically limited, suggesting specialized functions in mycobacterial physiology and pathogenicity.

The second phase of analysis was identifying a broad swath of functionally reactive enzymes in *A. fumigatus* that we cultured in nutrient-rich media/media supplemented with human serum. The latter was used to identify fungal response to the presence of human proteins. Multiplexed ABPP revealed significant changes in *A. fumigatus* metabolism and stress response during culture with human serum over time. It is likely that this pathogen adapts its metabolic activity within the host lung and fights immune host response by similar functions that we identified in human serum culture. We continued by comparing results with *A. fumigatus* to two closely related but non-pathogenic fungi, *Neosartorya fischeri* and *A. clavatus*. MABPP revealed several important biological functions and pathways upregulated in *A. fumigatus* compared to non-pathogenic organisms when cultured in the presence of human serum. As with earlier studies, environmental adaptation and metabolic response are key functions that facilitate the pathogenic capability of *A. fumigatus*. Importantly, we identified potential biomarkers of host infection, currently a desperate clinical need, as the most common, accurate method of post-mortem infection identification. Our findings in prokaryotic *Mtb* and eukaryotic *A. fumigatus* contribute to worldwide efforts to understand and eradicate these lung infections.

In FY 2013, we will focus on identifying probe-labeled peptides using our cleavable approach for both health and energy relevant research. For 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*.

PN10042/2284

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

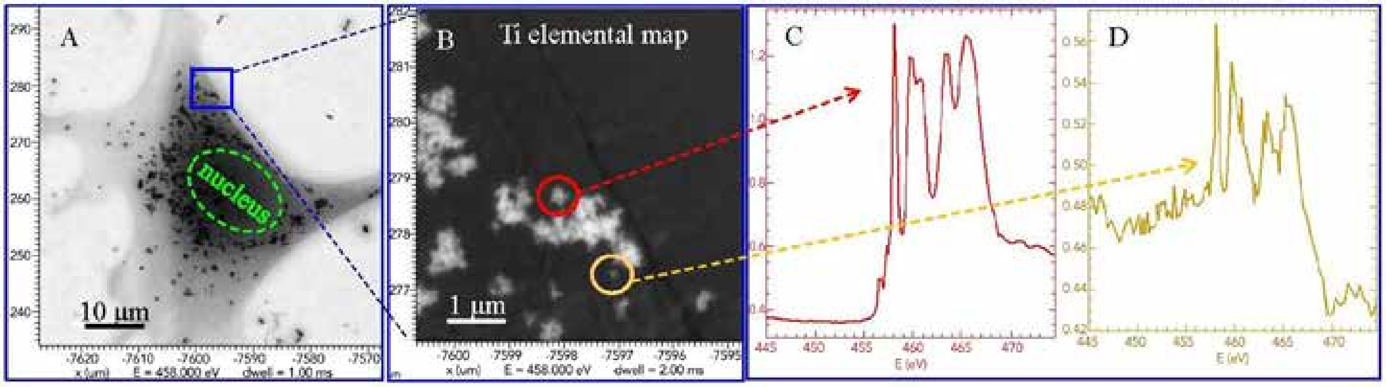
Galya Orr

We have been developing new integrated chemical and structural imaging approaches that will support investigating nanomaterial interactions with biological systems and polymers to enable and accelerate their safe applications in nanotechnology.

This project provides 3D high-resolution fluorescence imaging integrated with x-ray imaging and tomography for investigating cellular processes with nanometer resolution in the intact cell. This approach offers 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 a new understanding of their behavior and function in cell response and survival. Additionally, these efforts integrate chemical spectroscopy and imaging approaches to provide a better understanding of individual quantum dot distribution in the polymer matrix. In turn, this enables their use in solar energy applications with a focus on studying photo-induced variations in the electronic structure and energy level alignments that determine exciton formation, charge separation, and transport that essentially control the efficiency of the hybrid solar cells.

We commenced this project in FY 2011 by developing new imaging approaches to investigate individual nanoparticles and their interactions with living cells, providing the data needed to accelerate safe applications of nanotechnologies in industry and medicine. The unique properties of materials at the nanoscale have been explored for multiple applications, but the unknown impact of nanomaterials on human health and the environment has limited the use of these applications. The potential of engineered nanomaterials to impose adverse effects on living systems has been observed, but a great deal of confusion exists about the properties that make a particle toxic or biocompatible. Investigations of these relationships have been challenged by current limited research technologies and by the strong tendency of nanomaterials to agglomerate under experimental conditions, which leads to larger particles and provides information irrelevant to nanoscale materials and exposure *in vivo*.

Maximizing 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 3D chemical and structural images of individual nanoparticles within organelles in the intact cell with nanometer resolution. These methods have been applied to investigate the cellular interactions and fate of individual nanoparticles to identify toxic or biocompatible nanoparticle properties and delineate the underlying mechanisms. Also in collaboration with ALS scientists, we developed approaches to investigate individual nanoparticles in the intact alveolar cell to gain information about the chemical state of the particle in the intracellular environment. These approaches provide unprecedented understanding of the complex, reciprocal relationships between nanoparticle and cell. Using alveolar epithelial cells exposed to TiO_2 nanoparticles, we established experimental parameters for investigating this system with 20 nm resolution using scanning transmission x-ray microscopy



A. STXM images taken on the 11.0.2-beam line at the ALS, showing TiO_2 nanoparticles (black) accumulated in the peri-nuclear region;
B. Elemental map for titanium in the area marked by the blue square in A, showing structures of nanoparticle clusters with nm resolution;
C. and D. Spectra of a small cluster (red) and an individual nanoparticle (yellow), showing the titanium edge around 458 eV.

PN11043/2365

(STXM), including the growth of cells on 200 nm silicon nitride windows either when submersed in growth media or at the air liquid interface.

In FY 2012, we developed analysis tools specific to our questions. TiO_2 nanoparticles are relatively non-toxic but can be photo-activated to produce reactive oxygen species (ROS) that have potential to induce cytotoxicity. We currently expose cells to photo-activated particles to identify relationships between cellular response and particle properties, and determine whether and where in the cell-oxidative damage occurs. Ceria nanoparticles were reported to have protective and toxic effects, conflicting results that might reflect a shift from cerium^{+4} to a more active cerium^{+3} in different cellular environments. To investigate this possibility, we have been and will continue in FY 2013 to use STXM to determine the oxidation state of CeO_2 nanoparticles inside the cell and determine whether any changes occur in the surrounding intracellular environment. Positively charged nanoparticles are more toxic than negatively charged particles that are otherwise identical. To understand the underlying mechanism, we modified nanoparticles with primary or tertiary amines, both creating particles with positive surface charge but causing toxicity at different levels. We currently use STXM to determine whether the functional groups are shed or modified inside organelles to understand the differences in toxicity.

Mapping and Characterization of Organic Matter in Soil Aggregates using Laser-Ablation Sampling

M. Lizabeth Alexander

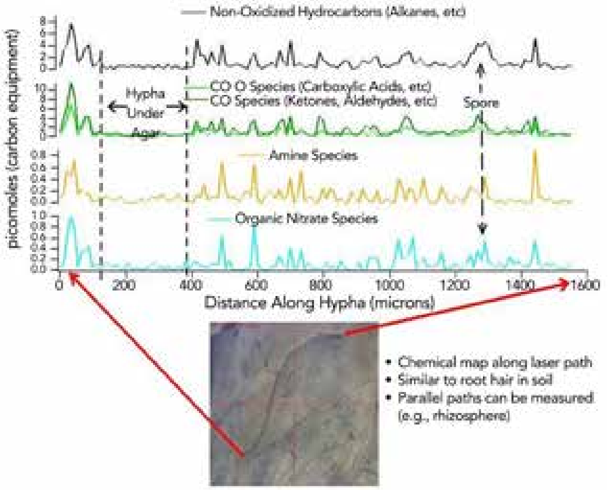
> ***We are applying existing technologies in new ways to examine the relationship between location of microbes, location of soil organic C, and the relative age of soil organic C at specific locations.***

C cycling in soil is primarily a function of microorganisms interacting with their environment. A true mechanistic understanding of C cycling in soil must occur at the sub-millimeter scale. Although critical to a picture of carbon cycling and relationship to climate change, current views of C deposition, microbial utilization, and sequestration of organic C in soil is based almost entirely on bulk sample analysis, with no clear understanding of underlying distributions and physical-chemical controls that occur at the micron-scale in intact soil aggregates. As most modeling approaches use empirical data collected at batch and field scales, direct transfer of these relationships into models may not adequately represent mechanistic processes nor may lead to correct model predictions in a perturbed soil system. An improved understanding of mechanistic drivers at the microscopic scale is highly appropriate, making it easier to scale up than to examine the larger, spatial-scale relationships.

The objective of this project is to apply existing technologies of LA-AMS and LA-CAS to study the speciation and spatial variation of C in soil. These sophisticated methods have the potential to overcome the problems of observation scale and soil opacity, and to map elements spatially and produce molecular information at a lateral resolution between 1-10 micron and depth resolution as little as 100 nm. This capability opens a variety of avenues for examining the relationship between location of microbes, location of soil organic C, and relative age (young/labile vs. old/recalcitrant) of soil organic C at specific locations.

A late FY start for this project, our focus has been on configuring the existing laser ablation instrument for the spatially resolved sampling of soil aggregates. The viability of LA-AMS for obtaining molecular speciation at a spatial resolution down to 10 microns has been validated on homogeneous soil samples. Fungal hyphae grown on an agar media were chosen as a test of the ability of LA-AMS to distinguish spatial variations in C speciation along the length of a single fungal hypha at a 10 micron resolution, yielding spatial distributions of chemical classes of C compounds corresponding to observed morphological variations. Recently, water-stable soil aggregates have been mounted, and optical imaging software required to perform LA-AMS has been validated. Data have been acquired for a single soil aggregate over an area of ~140 × 120 microns at a spatial resolution of 20 microns. Initial data are used to adapt existing software to create an image of C compounds as determined by the AMS. Ratios of C/N and other relevant quantities will be mapped as well. Progress has also been made on the LA-CAS system, with the primary focus on improving molar sensitivity to the 100 femtomole level to allow isotopic imaging at the level of habitats containing 10-100 microbes.

In FY 2013, we will complete development of the imaging software with our collaborators at the University of Colorado and Aerodyne Research. Data analysis will be automated to allow for generating near real-time chemical mages. Improvements to the LA-CAS system will be evaluated, and isotopic information from the LA-CAS will be integrated into the chemical images. 3D imaging will be performed in conjunction with x-ray tomography to construct spatial, chemical, and isotopic maps of multiple soil aggregates, which will improve understanding between the location of microbial mass relative to other carbon species and the role of morphology in those distributions. Isotopic distributions of C will be used to examine the hypothesis that the youngest C will be found at aggregate margins more readily accessible by oxidizing microorganisms and weathering reactions and at identifiable micro-aggregate interfaces where labile C binds micro- into macro-aggregates.



The linear distribution of several classes of carbon- and nitrogen-containing compounds obtained at LA-AMS at a spatial resolution of 10 microns. Total data acquisition time was under 10 min.

PN12047/2448

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

Rachel A. Bartholomew

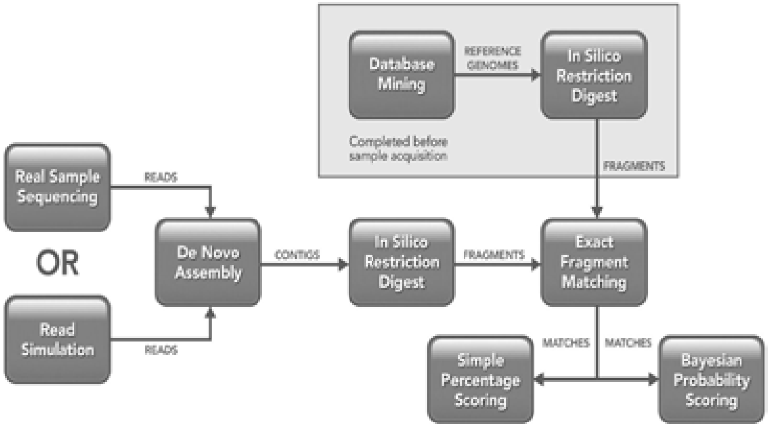
A major challenge to law enforcement and/or the first responder community is correctly identifying the unknown agent at a biological crime scene. One means of identification is through use of massively parallel DNA sequencing (MPS). The aim of our study is to develop and test computational tools for 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 took short MPS reads from a sample of an unknown organism, assembled these reads into contigs, and performed an *in silico* restriction digest to produce a set of sequence fragments. The ends of the contigs were not bound by restriction sites and were therefore not included in the fragment set. Identification was 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*



Analysis flowgram for massively parallel sequencing data.

168 MPS data (Illumina) resulted in high percentage matching (0.81) to the *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 more thoroughly, we used *dwgsim* in the freely available *dnaa* software packag e to generate simulated MPS data. This program produces simulated reads from a specified genome, allowing us to assemble and match these reads 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 incorporated the Bayesian calculations into the MPS bioinformatic toolsuite and demonstrated the power of the refined toolsuite on an expanded data set consisting of 24 *Francisella* genomes. Upon assembly and *in silico* restriction digest of the dataset, the fragments were matched back to the references genomes using the PNNL-developed toolsuite and other commonly used approaches such as Basic Local Alignment Search Tool (BLAST). While both methods gave the correct match, our method provided a higher metric of confidence in the match. Our toolsuite is faster than BLAST and, unlike other methods, can provide a confidence measure on an unknown genome's relationship to known genomes, and not just a contig or read. A manuscript detailing the toolsuite and MPS data analysis is in preparation for submission to *Nucleic Acids Research* online. Also in FY 2012, we generated MPS data using the SOLiD platform. Data analysis was performed by our collaborator Northern Arizona University (NAU) led by Paul Keim, a world-renowned *Bacillus anthracis* researcher. We anticipate a follow-on publication with NAU resulting from this data set.

Microbial Processes Accompanying Deep Geologic CO_2 Sequestration

Michael J. Wilkins

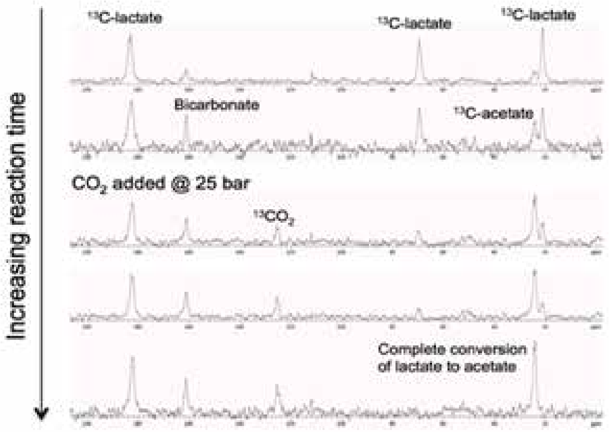
This project aims to increase understanding of the impact of geologic CO_2 sequestration on microbial biomass and viability. Deep subsurface locations for CO_2 storage contain microbial populations that may impact gas generation, caprock integrity, and other parameters that need to be better understood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

We have focused our current studies on the physiology and metabolism of a model subsurface sulfate-reducing bacterium (SRB), *Desulfovibrio vulgaris*. SRB are commonly found in deep subsurface environments that are promising locations for CO_2 storage. This research has leveraged unique experimental capabilities that PNNL has developed. High-pressure nuclear magnetic resonance (NMR) analyses of growing *D. vulgaris* cultures have been performed to determine the *in situ* metabolic state of these cells under varying CO_2 partial pressures. Biomass is incubated with ^{13}C-lactate solution that acts as a source of both carbon and electrons for growth; as the biomass utilizes this compound, increasing concentrations of daughter products (e.g., acetate, bicarbonate) can be monitored to determine rates of metabolism. To date, we have reproducibly demonstrated microbial growth in this system under both ambient (atmospheric pressure, 37°C), and pressurized (25 bar, 37°C) conditions. As this research progresses, the response of biomass to increasing pressures will be determined. Additional NMR experiments are also being planned utilizing a methanogenic (methane-forming) bacterium. These microorganisms can generate methane (CH_4) from H_2 and CO_2, and as such are of great interest in CO_2 storage environments where CO_2 will be in great excess and H_2 may be present from the fermentation of organic material. By using ^{13}C-labeled CO_2 we anticipate being able to track the activity of methanogenic bacteria under a range of pressures found in deep subsurface environments.

In tandem with high-pressure NMR investigations, the physiological state of *D. vulgaris* under elevated CO_2 pressures has been investigated at the mRNA level using a shotgun RNASEQ approach. A comprehensive suite of samples is currently being sequenced for metatranscriptomics; biomass was exposed to CO_2 pressures of 25 bar, 50 bar, and 80 bar before being flash frozen to preserve mRNA signatures that may indicate potential stress responses to CO_2 pressures. While preliminary data has indicated that some aspects of CO_2 stress response is shared across other stresses (e.g., pH, metal exposure), other up-regulated genes suggest that there may be some novel aspects to the cellular response. In particular, the up-regulation of a series of hypothetical genes warrants further attention. The sequencing of additional metatranscriptomic samples will allow gene network responses to be elucidated and may reveal roles for specific poorly annotated genes.

During FY 2013, our plans involve the analysis of metatranscriptomic datasets, continued experiments utilizing both SRB and methanogenic strains in tandem with high-pressure NMR, and the pursuit of collaborative research opportunities in this field that may lead to programmatic funding.



A temporal series of NMR scans showing the utilization of lactate by D. vulgaris and conversion to acetate and CO_2 (as bicarbonate) under 25 bar CO_2 at 37°C.

PN11052/2374

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

Michael J. Wilkins

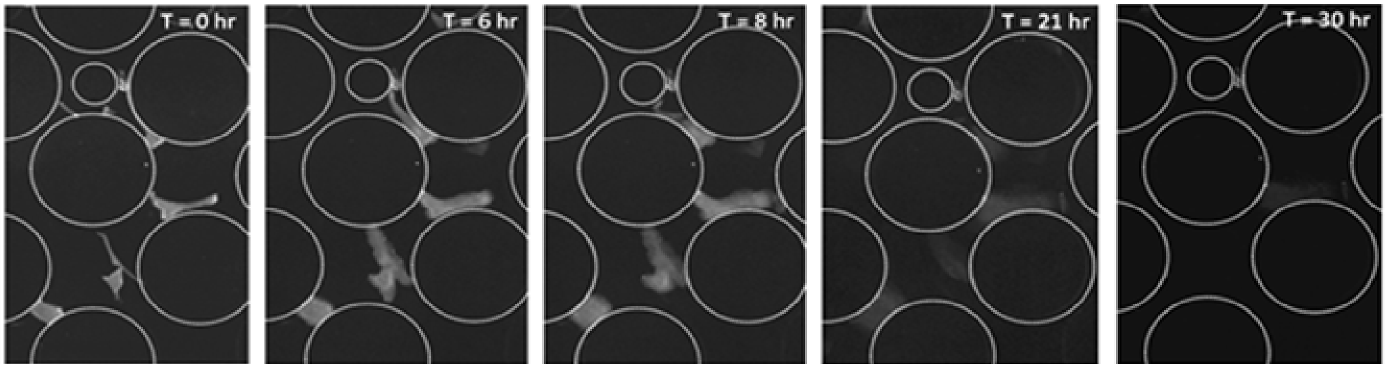
This project uses novel microfluidic platforms coupled with multi-modal imaging technologies to investigate microbial cellulose degradation at the pore scale. A better understanding of soil carbon flux is key for development of modeling tools for predicting carbon cycling in the environment, with implications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

Cellulose is 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, subsurface, oceans, plants, and soil, with microbial communities mediating many of the transformations between reservoirs. The flux of microbially-generated CO_2 from soil to 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 has an order of magnitude larger than anthropogenic fossil fuel combustion. Approximately 10% of atmospheric CO_2 cycles through the soil annually, yet the temporal and spatial dynamics of soil respiration remain difficult to model or predict.

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 the 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 the processes occurring at this pore scale in a non-destructive manner. Understanding these pore-scale microbial processes affecting the 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, with technologies arising from a number of other projects being integrated into these data sets. 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
- 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.



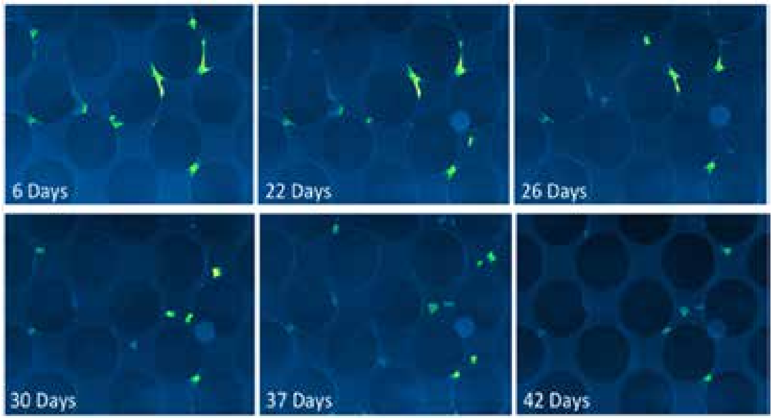
Cellulose deposits (white) degraded over a 30-hr period by the action of a cellulose enzyme mixture under constant flow conditions.

PN10055/2297

In FY 2012, our work focused on tracking the degradation of cellulose within the microfluidic pore networks, and monitoring bacterial growth associated with this carbon utilization. Significant progress has been made in developing these experimental areas:

- Cellulose nanocrystals that are spatially distributed into “resource islands” within the pore networks have been degraded using cellulose enzyme mixtures (Celluclast) for over 30 hours. These studies in heterogeneous pore networks have suggested that deposited cellulose in regions of the model that are exposed to lower flow rates may be more resistant to degradation by the enzyme cocktail, although the precise mechanism for this observation is as yet unknown.
- A common soil microorganism *Flavobacterium johnsoniae* was been inoculated and grown within these pore networks. These experiments have progressed over a period of several weeks that include multiple growth cycles. Over this period, little cellulose degradation was observed, suggesting that these cells were able to survive by utilizing only a very small fraction of the total C within the pore network. Calculations of the mass of C needed to support this biomass supported this conclusion.
- Another common soil microorganism *Cytophaga hutchinsonii* was inoculated into a pore network, and appeared to show more activity against the cellulose deposits. Over 30 days, cellulose was partly degraded, and then mobilized within the pore spaces. These species are thought to produce more cellulose enzymes than *F. johnsoniae*, and may explain the cellulose degradation observed in this experiment.
- An environmental enrichment was started using a Palouse soil sample as a starter inoculum in Dubos media with cellulose nanocrystals as the carbon source. This enrichment was able to degrade some of the cellulose, and cause aggregation of the remaining cellulose, potentially within a biomass-extra polymeric substance matrix.

These achievements to date have set the foundation for continued studies on cellulose degradation, with a focus on determining rates of cellulose degradation within specific regions of the pore networks. In the near-term, we aim to utilize the environmental enrichment culture (described earlier) within these experiments to determine cellulose-degradation rates using indigenous microorganisms. 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. Additional higher resolution imaging of labeled cellulose nanocrystals using a new microscope 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.



Cellulose degradation within a pore network that was inoculated with the common soil microorganism *Cytophaga johnsonii*. Cellulose deposits (green) decrease in size over time before being mobilized by advective flow and move through pore spaces. Biomass is not visible in this series of images.

PN10055/2297

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

Vanessa L. Bailey

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.

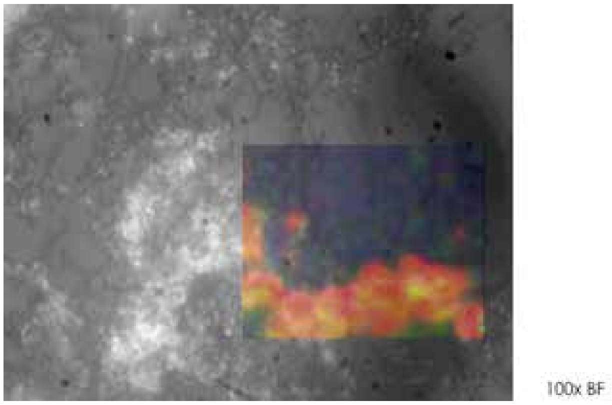
Microbial communities are difficult to study. Fundamentally, they are a complex network of cells that interact at various scales to mediate a wide range of metabolic processes. In short, they are often treated as “black boxes” in the environment, in that substrate goes into the community and various 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 the 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 has been 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) 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 vegetative and spore states.

Raman spectroscopy and subsequent statistical analysis of spectra distinguished the different microbial species and forms. A principal component analysis 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% and 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. These results were published in the journal *Analytical and Bioanalytical Chemistry*.

In FY 2012, we examined a mixed cultures consisting of roughly equal abundance of the three isolates di181, di202, and di307 and again used Raman spectroscopy to nondestructively map the microbial community. There was excellent agreement between the maps derived directly from the Raman spectra and those obtained from PLS-DA; however, only PLS-DA is able to discriminate between the di202 and di307 isolates.



Magnified white light image of selected region of mixed isolate dry mount. Inset shows the Raman spectral mapping resulting from the peak identification. Red=di181, green=di 202, or di 307, blue=glass slide. PLS-DA maps indicate that green is predominately comprised of di202.

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

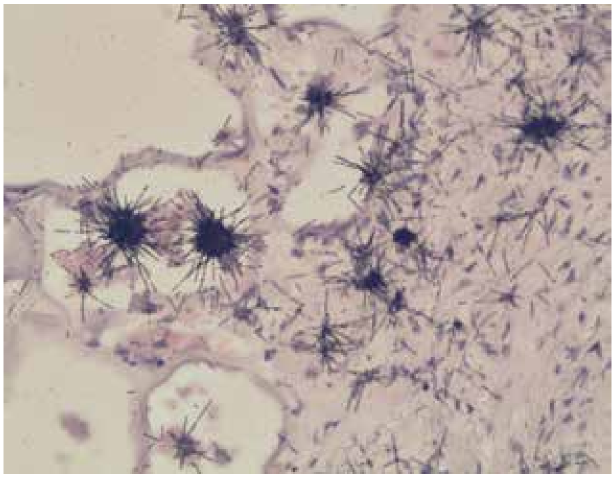
William F. Morgan

Given concerns for human exposure in radiation-contaminated cleanup areas (e.g., the Hanford Site and Fukushima), the increasing use of radiation in medicine and industry, and the potential for dirty bombs and other forms of nuclear terrorism, we are analyzing archival studies performed to understand the potential health effects from radiation exposure in a large animal model system. Further, we are comparing the results to occupational and accidental exposures of nuclear workers in an effort to understand the biological effects of exposure to ionizing radiations, with an emphasis on internal-emitting radionucleotides.

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 ($2 billion in today's dollars), 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 information collected represents a unique resource; significantly, data from these animal studies can be compared with information obtained from humans accidentally or occupationally exposed to ionizing radiations. Several of these individuals have voluntarily chosen to donate their bodies to science.

The long-term retention of inhaled soluble forms of plutonium raises concerns as to the potential health effects in persons working in nuclear energy or the nuclear weapons program. The distributions of long-term retained inhaled plutonium-nitrate [^{239}Pu (NO$_3$)$_4$] deposited in the lungs of an accidentally exposed nuclear worker (Human Case 0269) and in the lungs of experimentally exposed beagle dogs with varying initial lung depositions were determined via autoradiographs of selected histological lung, lymph node, trachea, and nasal turbinate tissue sections. These studies showed that both the human and dogs had a non-uniform distribution of plutonium throughout the lung tissue. Fibrotic scar tissue effectively encapsulated a portion of the plutonium and prevented its clearance from the body or translocation to other tissues and diminished dose to organ parenchyma. Alpha radiation activity from deposited plutonium in Human Case 0269 was observed primarily along the sub-pleural regions while no alpha activity was seen in the tracheobronchial lymph nodes of this individual. However, relatively high activity levels in the tracheobronchial lymph nodes of the beagles indicated that the lymphatic system was effective in clearing deposited plutonium from the lung tissues. In both the human case and in beagle dogs, the appearance of retained plutonium within the respiratory tract was inconsistent with current biokinetic models of clearance for soluble forms of plutonium. Bound plutonium can have a marked effect on the dose to the lungs, and any subsequent radiation exposure has the potential increase in cancer risk.

For this study, we have completed the pedigree analysis of irradiated dogs to investigate the potential for 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. A part of this study serves as a student's Master's thesis, and some of our results have been published in *Radiation Research*.



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.

PN10057/2299

Multiscale Simulation of Microbial Carbon Transformation in Soils: Connecting Intra- and Inter-Aggregate Scales

Haluk Resat

The objective of this project is to develop multiscale modeling approaches to link the dynamics of microorganism communities acting within environments that vary at very small scales (within individual soil aggregates) to the controls exerted by inter-aggregate flow and transport.

The Earth's soils represent a major pool of carbon in the global carbon cycle, estimated to be larger than the amount of carbon in the atmosphere and double the amount stored in vegetation. Soil microorganisms play a major role in the terrestrial carbon cycle, primarily by degrading recalcitrant forms of carbon such as polymeric cellulosic materials into more readily accessible forms that ultimately lead to the release of carbon dioxide during respiration and the release of methane during one type of anaerobic metabolism. Development of multiscale models that link the dynamics of microbial communities acting within micro-scale environments to the controls exerted by flow and transport at larger scales is necessary to improve our understanding of the factors that control the rates of microorganism mediated carbon turnover in the soil carbon pool. Therefore, ability to quantify the impacts of environmental conditions on soil microbial communities and understanding the factors that control the rates of carbon turnover in the soil carbon pool are needed for selecting management practices that maximize carbon storage within soils.

Bacteria-facilitated soil carbon transformation dynamics studies often focus either on the microscale ("the world microbes see;" for example, specifically within a single pore or soil aggregate particle) or at the bulk scale where the system is homogenized and kinetics are averaged over thousands to millions of pores and soil aggregates. Microscale simulations are not able to adequately represent within the larger pore network the effects of the variability between different soil microenvironments and the flow of water and associated transport of nutrients and microbes. Therefore, they cannot provide the large-scale information needed for estimation of overall rates of carbon cycling. On the other hand, macroscopic (averaged) simulations are not able to adequately represent the mechanistic dynamics of microbial communities and their interaction with microenvironments. A multiscale approach that links these two scales is necessary to identify environmental factors that might be controlled to manipulate carbon transformation in soils.

Progressive upscaling scheme to construct multiscale models for microbe-facilitated carbon cycling in terrestrial ecosystems.

For our project, the new models and associated simulation capability will be built by coupling our individual-based, aggregate-scale, saturated soil model of carbon-degrading microbial communities to pore-scale models that can accommodate both partially-saturated flow and nutrient transport. Computational methods that couple intra- and inter-aggregate soil processes have different requirements for full saturation (one fluid phase, water only) and partial saturation (multiple fluid phases, air, and water) conditions. That is, there are several different numerical methods that are required to study these cases. This project will therefore pursue a two-pronged approach that will allow us to make rapid progress using existing prototypes for different computational requirements that were developed previously by our groups.

This project started late in FY 2012 and has been active for only 2 months. Progress during this period can be summarized as the development of whole, aggregate level models based on individual-based study results has been initiated, and the work on modifying the smoothed particle hydrodynamics software for pore scale flow calculations to include microbial reaction kinetics has commenced.

During FY 2013, developed approaches will be used to investigate the hypotheses that in partially saturated micro-aggregates, co-existence of air and water filled pores causes patchy bacterial growth between anaerobic and aerobic organisms according to local carbon and oxygen availability. In addition, because of capillary effects, typically larger inter-aggregate pores are expected to drain before the smaller intra-aggregate pores during soil drying. This situation will create air-water interfaces near the surface of the aggregates, making those areas more favorable growth regions for aerobic organisms under partial saturation conditions.

PN12052/2453

Next Generation Software for Automated Structural Identification of Metabolites

Lars J. Kangas

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

There were multiple goals and challenges for this project in FY 2012. We aimed to develop a method to calculate charge locations in molecules. The software algorithm generates *in silico* spectra; knowing charge locations allow it to generate more accurate spectra, which would in turn enable more accurate metabolite identifications. A method was designed and tested using the NWChem software to compute Gibbs free energies for molecules, and from that the proton affinities that provide information about what atoms in molecules are more likely to be protonated to give the molecules a charge.

Specifically in FY 2012, we adopted the software to process NH_4 adduct molecules, not just the protonated molecules from the previous year. We extended the software by adding non-lipid metabolites to our development set. This increased the molecules in our dataset from 97 to 314. This new metabolite data came from metabolite standards that had been analyzed at PNNL. In addition, we requested and received the large metabolite database from the National Institute of Standards and Technology to add to our dataset. We are also promised to receive another dataset from Colorado State University as this data are generated in 2012. Another effort in FY 2012 has been to generate chemical reaction templates that are used in the software to configure correctly all atoms/bonds in molecules that experience bond cleavages in our software simulation of a mass spectrometer.

PN10061/2303

Optofluidics and Microfluidics for Exploring Biofuel Production at the Single Cell and Molecule Levels

Andreas E. Vasdekis

This project will measure biofuel production rates at single (or controlled number of) cell and molecule levels. At these levels, cellular process timing and details are uniquely revealed, and better-performing traits are unmasked.

Our society's prosperity and growth is heavily based on accessing reliable energy sources. Due to climate changes, increasing energy demands, and finite fossil fuel reserves, sustainable growth necessitates further developing renewable energy sources, which can be solar-, wind-, or biofuel-based. The latter (e.g., biodiesel and ethanol) are especially critical to our current transportation infrastructure. However, even if our understanding of these processes has substantially advanced during the past decade, there is still a lot to understand related to efficiencies of and tolerance to these alternatives.

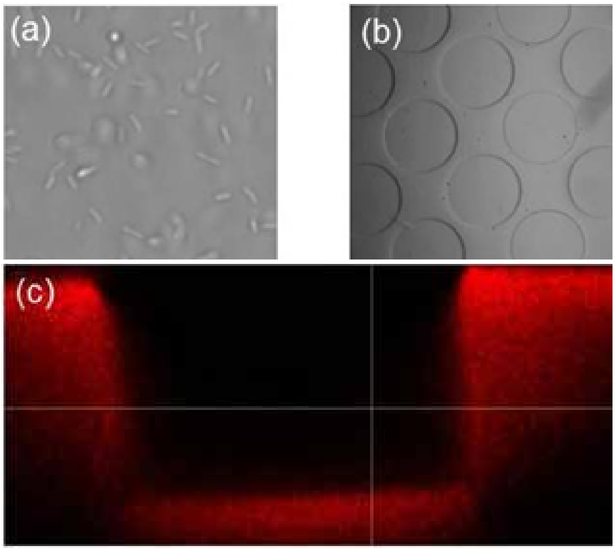
The present proposal explores biofuel production of a controlled population of cells and enzymes down to the single entity level. In this way, structural or temporal behaviors will be unmasked, where these behaviors become otherwise inaccessible in bulk studies. By applying single cell or molecular technologies to energy, fuel production kinetics will be extracted, as well why certain species behave better than others. The project's methodology is based on micro- and nanofluidics for cell handling and trapping, chemical imaging of interaction kinetics, as well as integration to active omic research platforms at PNNL.

Since the project's commencement approximately halfway into FY 2012, progress has been made on selecting microorganisms that are efficient in interacting with the environment, as well as identifying the interaction type that is strong enough to be detected by chemical imaging at high temporal resolution.

With regard to microorganisms, cellulose degrading and glucose processing microorganisms have been identified for research in microbial communities at PNNL (e.g., *Cytophaga hutchinsonii*) as well as at the Center for Bioproducts and Bioenergy at Washington State University (e.g., yeast). Micro- and nanofluidic assays capable of trapping single such cells or their controlled population number have been designed for these specific cell types based on previous experience with *E. coli*. Appropriate high resolution lithographic methods have been identified, along with gas impermeable materials (e.g., thermoplastics) for controlling the microenvironment of anaerobic processes.

For the chemical imaging of cell-environment interactions, non-linear approaches have been assessed thus far. Raman micro-spectroscopic studies have been initiated, which primarily focus on minimizing the noise contribution from surfaces. A parallel strategy involves the fluorescent imaging of labeled cellulose as well as time-domain lifetime imaging. In the latter approach, methods to integrate oxygen sensing chromophores efficiently in the microchannel have been designed, and initial tests show that the chromophore distribution can be controlled in three dimensions, in contrast to the planar (i.e., 2D) films that have been employed to date.

For FY 2013, single cell trapping in micro- and nano-fluidics will be performed. Trapping circuits in PDMS and polystyrene will be fabricated and tested. Cells that do not strongly adhere to surfaces and exhibit strong environment interactions will be selected. In addition to thermal nanoimprint modling methods, the alternative, more rapid techniques for plastic microfluidic and nanofluidic circuit fabrication will be identified. Cell-environment interactions will be imaged either in fluorescence or non-linear optical mode. In parallel, assays for mapping the interaction between enzymes and substrates will be designed and fabricated, and the possibilities of 'omic analysis in few or single cells will explored and assessed.



(a) Cytophaga hutchinsonii with an average length and width of 3 µm and 1 µm, respectively; (b) an imprinted microfluidic channel in polystyrene; (c) a fluorescent (and O_2-sensing) film integrated on a polystyrene microchannel.

PN12005/2406

Predicting the Response of Complex Biological Systems

Karin D. Rodland

This project integrates data from multiple imaging and mass spectrometry (MS)-based technologies to predict complex biological system response to external stressors. In addition to furthering PNNL's capabilities in systems biology, we will explore applications relevant to human health.

Recent technical improvements in genomics, high-throughput proteomics and transcriptomics, and other analytical technologies provide biologists with powerful tools for describing the behavior of simple cellular systems. What has been missing is predictive capabilities that allow manipulation of biological systems for desired outputs in bioenergy, bioremediation, and mitigation of harm in response to stressors such as ionizing radiation. Achieving this predictive capacity will require both continued technological improvements in experimental systems and in analytical tools, including imaging and developing new computational approaches and mathematical models that allow molecular-level data to be scaled to cells, cell communities, tissues, and organisms. The goal is allowing us to predict, manipulate, and potentially design multi-cellular systems that contribute to DOE goals in bioenergy, contaminant fate and transport, carbon sequestration, and global climate change.

This project applies unique PNNL capabilities in 'omics measurements, imaging, and computational modeling and simulation to promote the transition of biological science from merely describing biological phenomena to predicting, and eventually controlling, the response of complex biological systems to perturbation, whether in the form of environmental stressors, changes in climate, or deliberate manipulation to enhance performance (e.g., production of biofuels). Chief among the capabilities required are improved imaging systems that incorporate PNNL strengths in MS, nuclear magnetic resonance (NMR) spectroscopy, and emerging strengths in chemical imaging; one of the specific subtasks in this proposal focuses on combining mass spectrometry and NMR to provide a 2D image of biochemical changes in the brain. Integrating and interpreting data that arise from such combined imaging modalities will require application of novel computational tools for registering and adjusting multiple inputs. While existing research has often focused on very simple model systems consisting of one organism or cell type, it is increasingly clear that predicting the behavior of real biological systems requires model systems the incorporate realistic levels of cellular complexity, while allowing accurate measurement of individual components. Application of systems biology tools to such complex model systems is another goal of this project. Finally, if the goal is prediction of response, then there is an urgent need to apply new computational tools that can accurately simulate the behavior of complex biological systems over time and space, and then extrapolate to predict the response to perturbation.

During FY 2012, predictive capabilities successfully developed under this project include integrating 2D and 3D imaging technologies to understand spatial factors in biological function; identifying modifications to proteins that monitor the response to oxidative stress to predict changes in function or disease; developing unique nanomaterials for targeting medical isotopes; developing bioreactors for co-culturing of aerobic and anaerobic organisms; and applying activity-based protein profiling to understand developmental changes in enzyme function. The specific tasks undertaken in FY 2012 and their outcomes are described below.

Multi-modal imaging of complex biological systems. We applied unique PNNL capabilities in imaging MS (nanoDESI and MALDI) to identify the specific brain regions affected by exposure to neurotoxicants. In addition, we demonstrated high spatial resolution (12 μm) and sensitivity (0.2 fmol).

Characterize the protein modifications indicative of inflammatory responses. For this task, we first demonstrated the ability to detect and quantify multiple brominated proteins produced following activation of an immune response. Next, we identified autoantibodies that are indicative of cellular destruction in Type I diabetes. Finally, we have demonstrated the ability to detect and quantify addition of glutathionine to proteins as a mediator of inflammation.

Develop and test nanomaterials for delivery of medical isotopes in radioimmunotherapy. We produced antibody-conjugate $MnFe_3O_4$ nanoparticles and loaded them with Ra-223. In addition, we obtained data on leaching of Ra-223 from nanoparticles in relevant biological matrices.

Develop a bioreactor capable of co-culturing anaerobic bacteria and aerobic host cells. We demonstrated the ability to co-culture aerobic host cells (human intestinal epithelial) and commensal bacteria (*Lactoacillus reuteri*) in a 3D culture system. We also engineered a membrane system to maintain differing oxygen concentrations on either side of a bioreactor.

Determine changes in detoxifying enzymes in early development to assess risk of fetal and neonatal exposure. We developed activity-based probes for the enzymes that detoxify polycyclic aromatic hydrocarbons and measured the activity of these enzymes in early and late neonatal stages and in mature mice, demonstrating decreased detoxifying capability in the very young.

PN12061/2462

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

Stephen J. Callister

We are developing chemical or activity-based proteomics probes and bioinformatics approaches for discovering enzymes relevant to biofuels production via insoluble cellulose degradation. These developments will 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 developing second-generation biofuels. The enzymatic makeup 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. The enrichment of these enzymes and analysis using mass spectrometry will allow for the discovery of novel cellulose degrading enzymes and enable measuring the redundancy of these enzymes within a microbial community.

PN10069/2311

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. While the first probe design is not original, working out the synthesis steps to make this probe was challenging and represents a breakthrough to enable 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. For FY 2011, a total of 13 probes were chemically synthesized, designed generally to target glycoside hydrolysis activity, and have anticipated specificity for exo- and endo-gluconases as well as β-glycosidases. Testing was initially performed on commercially available glycoside hydrolase enzymes, with several tests used to evaluate each probe. 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.

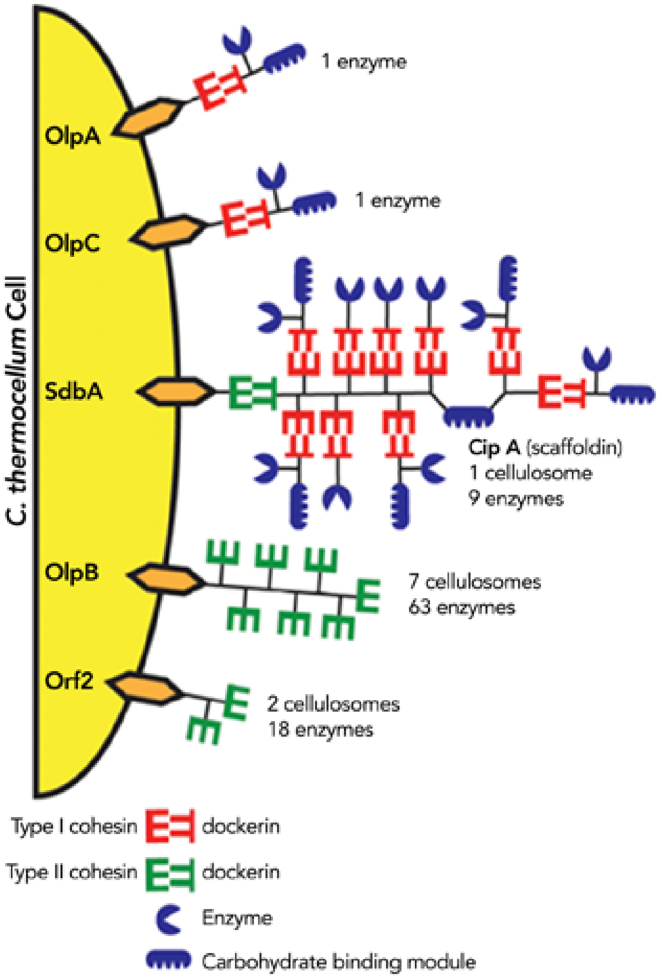
In FY 2012, two cellulose degrading bacteria, *Clostridium thermocellum* and *Fibrobacter succinogenes*, were chosen to test probe selectivity. Each bacterium was cultured on a growth media containing glucose and cellulose. Complex protein mixtures secreted to growth media and found within cell biomass were extracted and labeled using each probe for *C. thermocellum* and a subset of probes for *F. succinogenes*. Samples of labeled proteins and unlabeled proteins were then analyzed using mass spectrometry to supply protein identifications. Results from the application of probes to *C. thermocellum* are currently being written up for scientific publication, while the data acquired for *F. succinogenes* are being analyzed with help from a University of Wisconsin-Madison laboratory. Depending on the probe, a range of proteins (41 to 219) selective for carbohydrates were identified, including 7 proteins having an undefined role in cellulose processing. The enrichment of these 7 proteins using these probes from the complex protein mixture could aid in hypothesis development concerning their role.

The implementation of algorithms for analysis of liquid chromatography mass spectrometry probe data and global proteomics data derived from microbial communities have been completed, and a scientific paper describing these algorithms has been submitted for peer review. These algorithms are part of 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, and a trace-back capability that allows the targeting of important mass and elution time features for tandem mass spectra data generation, if tandem mass spectra were not generated. Tandem mass spectra are critical for peptide sequence assignment and protein identification. These bioinformatics enhancements are significant in that they allow the proteomics analysis of both probe labeled proteins and complex protein mixtures from microbial communities without the initial need of genomic sequence information.

In addition to testing the chemical probes against known cellulose degrading organisms present in a liquid culture environment, tests were carried out on the ability of the probes to label carbohydrate active enzymes within the soil environment. Crude extracts of the important cellulose degrading fungi *Trichoderma reesei* were added to a soil and successfully labeled. The action of native cellulases in the soil is a critical component in the cycling and sequestration of carbon. Testing of the probes' ability to perform in the soil is ongoing.

To test whether functional redundancy correlates with the stability of cellulose degradation, a systematic perturbation of cellulose degrading anaerobic microbial communities housed within engineered bioreactors has been undertaken. This experiment comprised of sampling a parent and daughter bioreactor to assess natural variability in cellulose degradation prior to the onset of a temporary pH adjustment in the daughter bioreactor. During this perturbation and just following the re-establishment of pre-perturbation bioreactor conditions, several measurements were made, including enzyme kinetics, volatile fatty acid production, and gas production. Samples were also collected for proteomics analysis. During the next stage of the experiment, the volumetric flow rate through the bioreactor was increased, altering the population makeup of the microbial community and theoretically altering the functional redundancy. Finally, the same pH adjustment was again applied to the daughter reactor, and samples were collected as described above. pH is a critical environmental factor in maintaining a healthy anaerobic microbial community.

During FY 2013, measurements made during the bioreactor experiment will be analyzed and data generated from the samples collected for proteomics analysis. Additionally, the use of MultAlign will play a critical role in this analysis for measuring differences in functional redundancy.



The cellulosome of *C. thermocellum* is composed of several proteins involved in the degradation of cellulose. The chemical probes synthesized as part of this research project are designed to label and enrich these proteins from a complex mixture of proteins not involved carbohydrate enzymatic activities.

PN10069/2311

Pulmonary Injury from Acute Events Related to Nuclear Energy Production

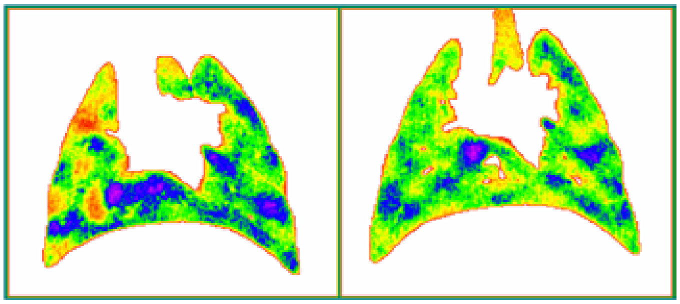
Rick Jacob

This project will develop state-of-the-art imaging to enhance understanding a range of radiation exposure effects on pulmonary mechanics to facilitate development of timely, effective treatments in clinical and emergency response.

Catastrophic events such as that in Fukushima, Japan can result in significant radiation release and exposure to plant workers and large populations. Most studies of pulmonary radiation exposure effects have focused very long-term cancer occurrence from low-dose medical exams or acute tissue damage from high-dose radiation oncology. Few studies have examined radiation exposure impact on whole-organ mechanical function, which is critical to gas exchange. Recent work at PNNL suggests that lung disease that is not detected by conventional imaging or histology can induce mechanical changes that may be detected using a new dynamic imaging approach.

The objective of this project is to develop an improved understanding of the fundamental pulmonary mechanical changes due to radiation exposure. By studying animal disease models, we can begin to understand the effects of radiation on the lungs and develop a diagnostic approach translatable to humans critical to understanding the basic physiological response and disease course. We anticipate that this project will result in clinically translatable technical advances in dynamic pulmonary imaging and image analysis. This project will also develop a reliable animal model of lung radiation damage for future work of this nature.

Our initial task included examining a dose-response study to gauge the chronic response to a range of radiation doses.



Ventilation maps show air volume increase on a voxel-by-voxel basis (on a rainbow scale, warm colors show small increase, cool colors the greatest). Left: A coronal slice of a ventilation map calculated from the dynamic CT images of the lungs of a control rat. Right: A similar slice of a rat exposed to 15 Gy radiation. The ventilation heterogeneity in the control rat is higher than that of the irradiated rat, a possible indicator of radiation-induced lung disease.

PN12065/2466

The centerpiece of this year was the radiation exposure and four-dimensional computed tomography (4D-CT) imaging of 25 female Sprague-Dawley rats. The thorax was exposed to a one-time dose of 0, 6, 9, 12, or 15 Gy (n=5 each group) of gamma radiation from a 60-Co source. This was done in a blind fashion such that those doing the animal handling, experimentation, and data analysis were unaware of which animals were in each group. To facilitate exposure, custom holders were made that conformed to the rats' size and shape that enabled repeatable positioning in front of the beam. Also, a 12-inch-thick custom lead beam collimator was used to minimize collateral exposure.

During the 6 months between exposure and data collection, significant progress was made in image processing and analysis using existing 4D-CT data. In particular, pre-registration processing parameters and non-rigid registration were empirically refined through an iterative process. After 6 months, the rats were evaluated with two different pulmonary function tests (PFT): one measured breathing parameters in free-breathing unanesthetized rats, and the other measured lung mechanical properties using forced maneuvers in anesthetized rats. A new, whole body plethysmograph was acquired for the free-breathing PFT, and we received training on its use. Most importantly, 4D-CT imaging was performed at 100 ms temporal resolution on the live, mechanically ventilated rats, after which blood, bronchial-alveolar lavage fluid, and saliva samples were collected. Finally, the lungs were excised for analysis of collagen content and weight.

The most important finding of the current year's work is that ventilation maps made from dynamic CT imaging were predictive of radiation dose. We found that map heterogeneity measured by the coefficient of variation correlated significantly ($p<0.05$) with dose level. Unexpectedly, the control rats showed higher heterogeneity than the exposed, with heterogeneity generally decreasing with increasing dose. Interestingly, CT image intensity, a conventional and clinical metric of disease (measured in Hounsfield units), did not significantly correlate with dose. With the exception of quasistatic chord compliance, PFTs also did not correlate with dose; the low-dose group showed the greatest variation from control in many PFT results. We observe that the 6-month time point represents only a snapshot in the dynamic, complex evolution of the poorly understood disease. It is also noted that the biomarkers have not yet been evaluated; nevertheless, our results suggest that dynamic 4D-CT imaging provides a sensitive indicator of subtle, radiation-induced lung disease.

In FY 2013, we will validate the radiation exposure and imaging at the 6-month and add a second 8-month time point. This will be done with a greater n, but we will only include the 0, 6, and 15 Gy dose levels. PFT data and biosamples will be collected as before, and histology will be added.

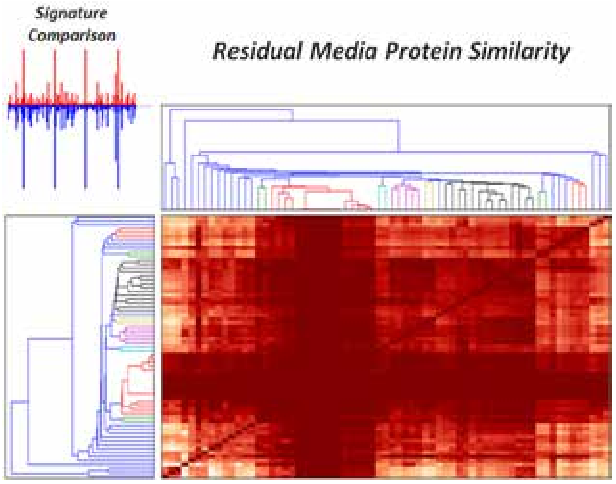
Statistically Significant Forensic Fingerprinting: Protein Analysis of Biological Agents

Brian H. Clowers

This effort aims to develop a framework and metric capable of statistically distinguishing between highly congruent forensic samples using residual growth medium protein profiles.

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 on 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.

Within the range of observed media proteins, this project leverages the frequency of amino acid observation for known samples which serve as an underlying, emergent signature to be employed for future sample comparisons. Each peptide feature is weighted based upon its relative frequency of observation across the entire media library and, within a given comparison, these weights provide a likelihood of a match between an unknown and a 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 rapidly identify statistically relevant matches across sample fingerprints.



Similarity matrix for observed protein signatures across different culture conditions. The clustering dendrogram highlights media formulations with high degrees of similarity based on residual media components. Detailed signature comparison provides a mechanism to validate manually calculated associations and peptide identification. Strong correlations exist between similar protein types demonstrating promise in a forensic setting.

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.

Applying our matching approach to a database comprised of 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. Using a similar approach in FY 2012, an additional strain of *Yersinia pestis* (lcr-) was cultivated using an extended set of media growth conditions compared to FY 2011. Using the peptide profiling and signature hashing approach a high degree of similarity was observed between protein profiles derived from preparations using similar starting materials. This exercise further demonstrated the ability of this approach to associate known media formulations with residual components found in a biological preparation.

During the second half of FY 2012, the signature curation, statistical algorithm, and database architecture were intenerated into a web-based interface that enables researchers and analysts to examine protein profile associations at all levels, including access to raw data. Using a range of internal and external sample resources, this effort has developed a flexible sample comparison framework. With emergent growth media peptide profiles as a demonstration case, a tangible forensic analysis tool developed at PNNL for the broader bioforensic community is specifically directed at use cases related to biothreat attribution.

PN11073/2395

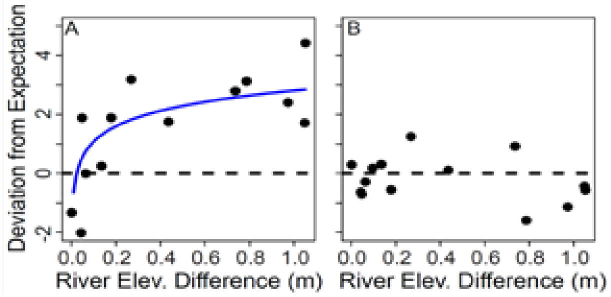
Understanding the Processes that Govern Subsurface Microbial Communities

James C. Stegen

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 between the observed change in microbial community composition (through time) and the expected change in composition given stochastic community dynamics. Horizontal axis: the change (through time) in the elevation of the Columbia River, which intrudes into the Hanford 300 Area subsurface at high river stage. Increasing deviations with increasing levels of intrusion (A) demonstrates that river intrusion can substantially shift microbial community composition. At a second site (B), there was no influence of intrusion. The two sites differ geologically, suggesting an important interaction between river intrusion and sediment composition.

Through FY 2012, this project focused on three major tasks as described in detail below.

Develop new statistical tools that quantify the influences of ecological processes and identify unmeasured variables that influence microbial communities. These tools were applied to a pre-existing dataset of microbial community composition from the Hanford 300 area subsurface. The results were collated into a conceptual model describing major features of the system (including an unmeasured variable) that govern variation in community composition.

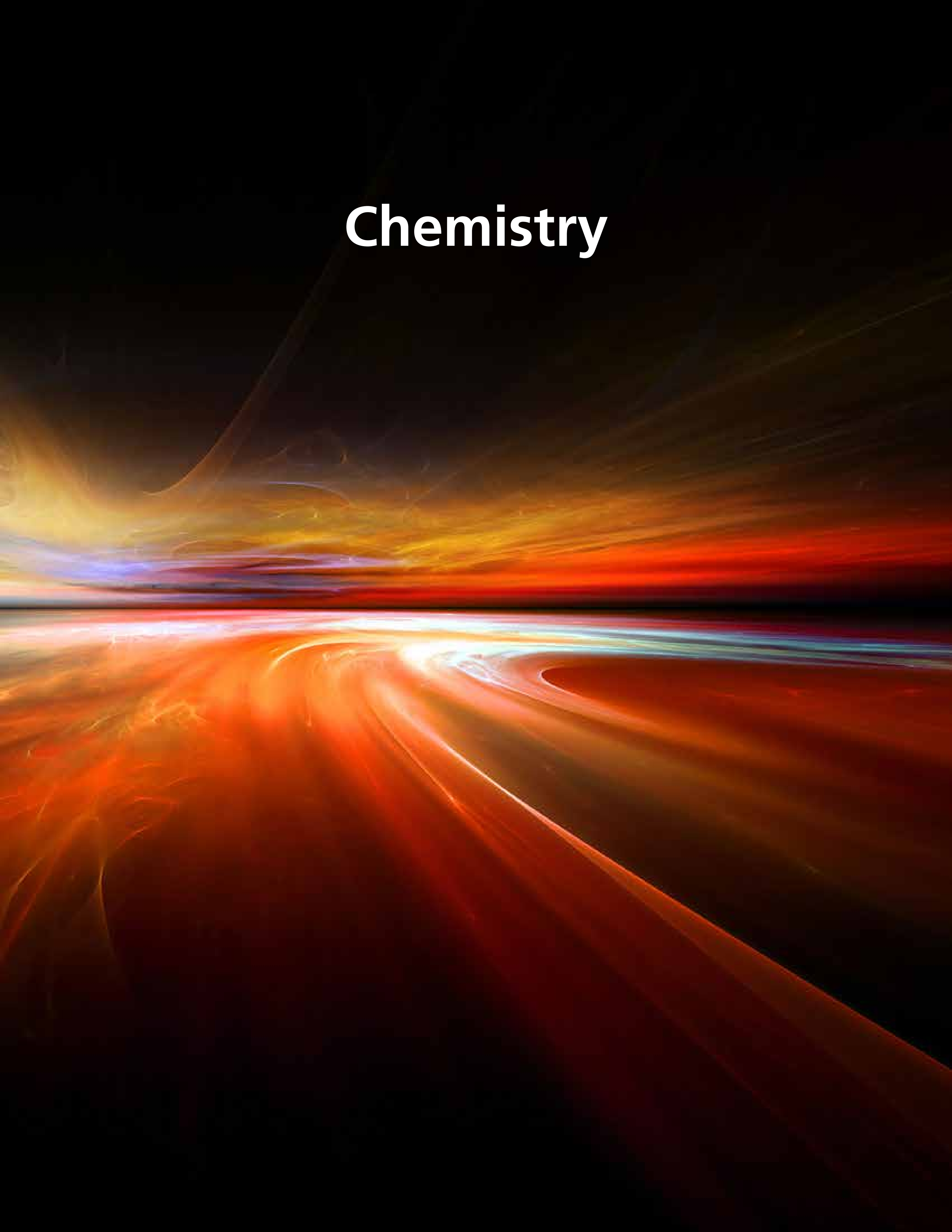
Develop new collaborations within and outside PNNL that focus on understanding factors that govern microbial communities. One new collaboration is international in scope, including researchers from China and Finland. The new statistical tools developed in the first task were applied to a broad range of ecosystems in comparative analysis. The new tools proved essential in arriving at robust inferences and we showed that across ecosystems microbial communities are governed by similar, deterministic processes. Two additional collaborations include an empirical study linking microbial biodiversity to ecosystem function and a simulation study aimed at understanding the processes that govern spatial biodiversity gradients.

Design and execute a large field campaign in the Hanford 300 Area that uses a multi-'omic approach to characterize spatial variation in geochemistry and microbial communities in terms of their composition and metabolic function. To date, we have four datasets that include metagenomic, metaproteomic, and GeoChip data. Additional samples (23) taken across a key environmental gradient have been collected and processed; the material from these will be analyzed within the context of a recently approved EMSL user proposal.

In FY 2013, we will continue to focus on understanding community composition through space and time and work toward predictive simulation models. In addition, we will interrogate existing dataset with additional novel statistical tools to characterize how species interactions influence microbial community composition. The data currently being generated will be evaluated to uncover linkages among microbial metabolic function, hydrological dynamics, and geochemistry. Information gained through these empirical studies will provide the foundation of simulation models used to predict spatial and temporal patterns of microbial community composition and metabolic function.

PN11078/2400

Chemistry



Biodegradable Linear Polycarbonates Through Catalytic Polymerizations of CO_2 Utilizing Switchable Ionic Liquids

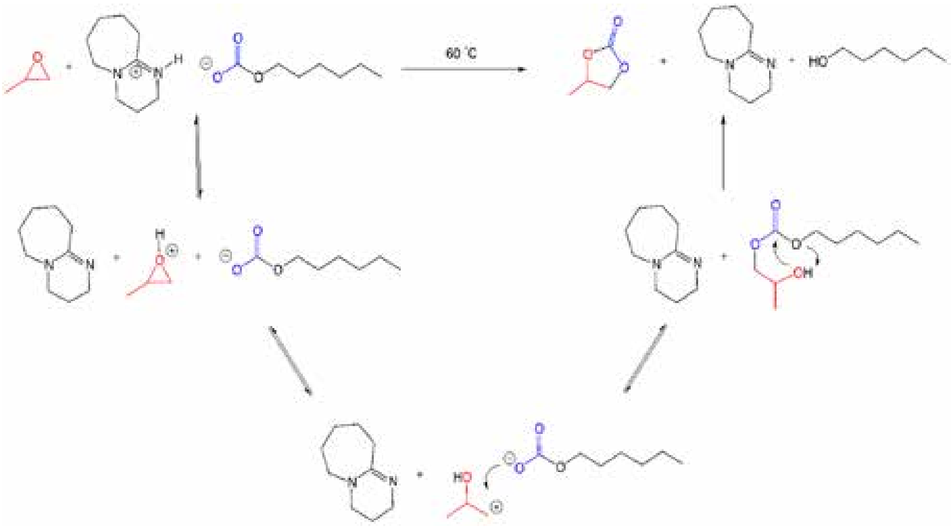
David J. Heldebrant

This project is exploring the direct use of CO_2 (chemically fixated) in CO_2-capture solvent systems toward developing more energy efficient and CO_2-neutral processes to produce plastics and fuels.

The objective of this project was to demonstrate that alkyl carbonate ionic liquids can be CO_2 mimics for CO_2 catalysis as they act as a CO_2 carrier, concentrator, and solvent, but most importantly as a chemical surrogate. Alkyl carbonate ionic liquids contain a 0.5 mole fraction of “CO_2” in solution, offering unprecedented concentrations of CO_2 at atmospheric pressure. In contrast, conventional catalysis using CO_2 requires high pressures (often > 50 ATM) to achieve such concentrations. Alkyl carbonate ionic liquids continuously capture and activate CO_2. Being polar, they allow stabilization of charged/polar intermediates common in catalytic reactions such as polymerizations. Alkyl carbonates are negatively charged, favoring complexation to homogeneous catalysts. The SP^2 hybridization of the alkyl carbonate enhances the electrophilicity of the central carbon, making it more reactive than neutral CO_2. Alkyl carbonates also are predicted to entail unique free energy profiles and likely new reactive pathways than to CO_2.

It was hypothesized that alkyl carbonates were could enhance catalytic polymerizations of CO_2 and epoxides. Such polymerizations require high pressures needed to provide the available [CO_2] in solution and suffer from chain termination of the growing polymer. Higher concentrations and activity of the carbonate could increase the kinetics but also the molecular weight of polymers. Chain termination occurs when polycarbonate chains backbite and cyclize to form kinetically and thermo-dynamically favored cyclic carbonates. Alkyl carbonates could retard backbiting by using an excess of alkyl carbonate in solution to trans-carboxylate to the catalyst or the growing polymer chain. Such a system could kinetically drown out the intramolecular cyclization thus enhancing molecular weight. Many groups have focused on studying advanced catalysts for polymerizations but the majority of them operate on CO_2 such that regardless of catalyst, the reactivity and selectivity are similar as the reagents and conditions are the same. The lone variable left to change in CO_2 catalysis is the CO_2 itself. Changing the reagent could alter reaction selectivity, kinetics and catalyst design, and open doors for new products that are unavailable starting from CO_2. Recently, the groups of Milstein and Samford have demonstrated just that, showing that carbonates can be hydrogenated directly to methanol, and their results prove that carbonates can be viable reagents in catalysis.

Polymerizations of alkylcarbonates and epoxides. Polymerizations of CO_2 and propylene oxide were performed with varied loadings of diazabiciclo[5.4.0]undec-7-ene hexylcarbonate [$DBUH^+$]$C_6H_{12}OCO_2^-$] ionic liquids using zinc glutarate and chromium salen chloride catalysts. Un-optimized chromium catalysts were chosen to determine if transition metal catalysts were tolerant of alkylcarbonate chemistry and to discern the difference in reactivity and selectivity between neutral CO_2 and alkylcarbonates. As expected, the Lewis acid catalyst zinc glutarate was deactivated regardless of alkylcarbonate loadings, which is attributed to alcohol poisoning of the catalyst. The transition metal chromium salen Cl was more tolerant of DBU and 1-hexanol but only if [$DBUH^+$]$C_6H_{12}OCO_2^-$] was formed prior to propylene oxide (PO) addition.



Proposed mechanism of metal-free propylene carbonate (PC) synthesis from alkylcarbonate precursors and PO.

The loading of $[DBUH^+]C_6H_{12}OCO_2^-]$ had a direct impact on the selectivity, isolated yield, and the molecular weight of produced polymer. Similarly to the observations of Darensbourgh with phosphine and azide co-catalysts, we find one catalyst equivalent of the alkylcarbonate the optimal loading with respect to isolated yield of polymer and selectivity toward PPC. Increased loadings of alkylcarbonate above two catalyst equivalents shut down the polymerization as PC began to be exclusively produced.

Metal-free conversion of alkylcarbonates and PO to PC at atmospheric conditions. If $[DBUH^+]C_6H_{12}OCO_2^-]$ is used in non-catalyst equivalent amounts the reaction exclusively favors the formation of PC in quantitative yield. At first we believed the catalyst participated in the production of PC, but the reaction proceeds at the same rate even in the absence of catalyst. Our results showed that PC is the favored product whether catalyst is present or not. The reaction between $[DBUH^+]C_6H_{12}OCO_2^-]$ and PO occurred at pressures as low as 1 ATM at temperatures as low as 40°C, albeit slowly.

We observed a mechanism consistent with acid promoted ring opening of PO by a proton transfer from $[DBUH^+]$ followed by ester formation, and subsequent cyclization of the ester to form PC The cyclization liberates 1-hexanol which can then further react with DBU and CO_2 to reform $[DBUH^+]C_6H_{12}OCO_2^-]$ and the cycle continues. The mechanism and reactivity of the alkylcarbonate towards epoxides was confirmed using molecular theory. As predicted the free energy pathways were lower for the alkylcarbonate than neutral CO_2 with respect to carboxylation chemistry.

The production of PC from an alkylcarbonate at 1 ATM of pressure in the absence of a catalyst has never been observed before. This program developed a new and cost-effective synthetic methodology to produce PC straight from CO_2 contained from a capture solvent. Ultimately, this chemistry was shown in this study to capture, concentrate, and convert CO_2 into useful products such as PC and potentially PPC polymers. While during this project we were able to show this unique reactivity only towards cyclic carbonate formation, we believe that the fundamentals of alkylcarbonate chemistry have been demonstrated, and our data will direct the development of catalysts that could utilize the reactivity of alkylcarbonates for polymerization reactions or other chemical conversions of CO_2 into value-added products, including fuels.

Characterization of Catalyst Materials in the Electron and Atom-Probe Microscopes

Ilke Arslan

With our current global business economy, fuel is extremely important for transportation by car, plane, and boat. The catalytic materials and processes studied in this project relate to the conversion of renewable and conventional energy resources to provide less expensive, more environmentally friendly fuel.

This project aims to advance and combine advanced techniques on the nanoscale to further the fundamental understanding of zeolite catalysts. The characterization-synthesis loop is an extremely important aspect of being able to design and controllably synthesize a material of industrial significance. The characterization on the atomic and nanoscales allows for fundamental understanding of the catalytic processes that aids in designing a better catalyst. We employ atomic resolution and 3D imaging as well as in-situ fluid imaging in the scanning transmission electron microscope (STEM) combined with atom probe tomography (APT). Chemical information can be obtained in the STEM using electron energy loss spectroscopy.

Much of the experimental analysis in this project will make use of the Z-contrast imaging technique in the STEM. To form a Z-contrast image, the scattered intensity (electrons) is collected at high angles and over a large angular range on a high angle annular dark field detector, averaging coherent effects between atomic columns in the specimen. This allows each atom to be considered to scatter independently with a cross section approaching a Z^2 dependence on atomic number (and hence the name Z-contrast imaging). This detection geometry yields an incoherent image where changes in focus and thickness do not cause contrast reversals in the image (unlike conventional TEM) so that atomic sites can be identified unambiguously during the experiment.

In electron tomography (ET), a series of images are taken at different tilt angles; the images are then combined using reconstruction algorithms to form a 3D representation of the nanomaterial. The application of ET to inorganic materials using STEM has developed rapidly. A fairly large range of volumes of material can be analyzed in 3D, for example as small as $10 \times 10 \times 10$ nm^3 to as large as $300 \times 300 \times 300$ nm^3, with the 3D resolution varying from just under 1 nm to ~5 nm depending on the volume size, number of images acquired, tilt range achieved, and alignment and reconstruction methods.

APT is a controlled field evaporation technique that produces sub-nanoscale spatial and concurrent chemical resolutions. However, a number of artifacts can limit the overall resolution. Knowing the 3D structure of the volume of material to be analyzed a priori by APT is therefore crucial. The most accurate way to do this is by matching in 3D with a non-destructive technique such as ET. The artifacts in APT and ET are in different directions; therefore, the artifacts of each method can be understood and compensated.

These methods are combined and applied to two sets of zeolite materials: MCM-22 and related layered zeolites that can be delaminated, and ZSM-5. MCM-22 is used as a precursor material for delamination, with the goal of pulling apart the zeolite sheets to provide a higher surface area while keeping the active sites on the surface intact. This higher surface area allows access for larger bulky molecules to create reactions, opening up the materials for new processes. These delaminated materials are useful for processes such as cracking, alkylation, and understanding the delamination process in 3D. ZSM-5 is being studied as the acid catalyst for the conversion of lignin-derived phenolic oil to produce gasoline range hydrocarbons and methanol. As this reaction occurs in water, it is important to understand the fundamental morphology and chemistry of the zeolites in water. We are applying a fairly new technology of imaging through fluids in the electron microscope to understand the structure of the zeolites in its aqueous environment. High resolution imaging and 3D ET will also be combined with APT to understand the location and density of Al atoms (acid sites) with nanometer spatial resolution.

The ultimate goal of delaminating zeolites is to investigate the formation of bimetallic clusters on supports from complexes of metals that are chemically similar to each other and have a strong tendency to form clusters. The family of metals is Fe, Ru, Os, Rh, and Ir. Suitable precursors are $Fe(acac)_3$, $H_2Ru(CO)_4$, and $H_2Os(CO)_4$, $Rh(CO)_2(acac)$, and $Ir(CO)_2(acac)$. The support for these metal clusters will be zeolites because a zeolite support allows precise control of the structures of supported metal clusters as a consequence of the regularity of their surfaces and cages and the opportunity to control the number of well-defined bonding sites (the metal precursors tend to react at the Al sites, as evidenced by EXAFS spectra).

One of the challenges of zeolites as support is determining structures of the metal clusters throughout the samples. An appealing alternative to bulk zeolites is zeolites in the form of extremely thin layers. The thin-layer zeolites have already caught the attention of microscopists, yet to our knowledge, there are no reports of images of small metal clusters in

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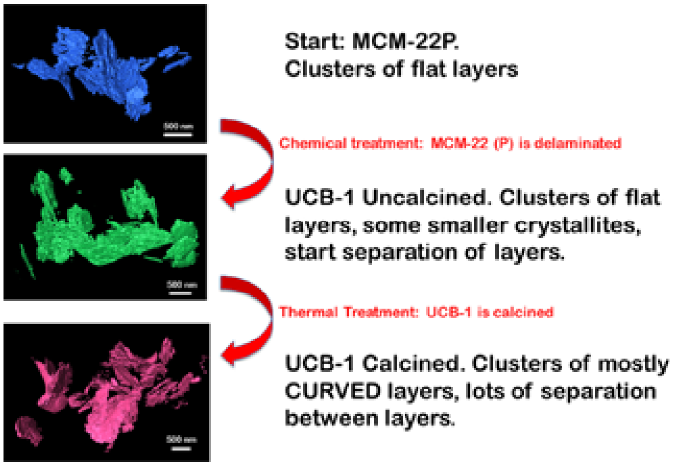
them. These ultrathin zeolites (some are exfoliated samples) are appealing supports for our clusters, and we expect to be able to obtain high-quality 3D images of the samples and atomic-resolution images of the clusters in them (and even of the zeolite frame), as all the clusters will be located near sample surfaces.

To realize this goal, the zeolite support must be fully characterized first in order to understand the morphology and determine whether the synthesis is successful. This is what we have focused on in the first year. We have done a thorough analysis of the 3D morphology of the zeolite at three stages of chemical and heat treatment to understand the delamination mechanism. To date, there has been no published literature on a direct and 3D visualization of the delamination process.



3D morphology of the zeolite at three stages of chemical and heat treatment

The synthesis is performed by the Katz group at the University of California-Berkeley. The starting material is MCM-22, a precursor material. STEM tomography was performed on this material, and it is found that there are many thin sheets of zeolite that are bound together in large, flat clusters. The distance between the sheets is the pore size, which limits larger bulky molecules from entering. The next step is a chemical treatment, which in this case is performed at pH 9 using an aqueous solution of cetyltrimethy-lammonium bromide, tetrabutylammonium fluoride, and tetrabutylammonium chloride at 353 K. Note that this is a much lower pH than zeolite delamination in the literature (pH 13), which yields no detectable amorphous areas that inhibit catalytic performance, such as those found in materials such as ITQ-2. The 3D imaging performed at this stage shows that the zeolitic layers are still flat and in clusters, but the distance between the layers is slightly larger, suggesting swelling and breaking of bonds between layers.

At the final stage of synthesis, the material is calcined. The heat treatment does something phenomenal in that the zeolite sheets come apart in curvy layers, and the surface area increases. The distance between clusters of the curvy sheets is larger (up to several hundred nanometers), thereby providing ample space for bulky molecule reactions. This is the first demonstration of a direct 3D visualization of the delamination process.

With the support synthesis established, FY 2013 research will focus on the synthesis of small metal clusters (~4 atoms) and their insertion into the zeolite. Their location on the zeolite surface will provide us with an indication of the active (acid) site densities and locations and will be a challenging task for both synthesis and characterization.

With zeolites for biomass conversion, we provided the first images of the ZSM-5 zeolite imaged in-situ in water. As expected, we find that the cluster size of particles when suspended in water is smaller than when the material is dried. Upon analysis of ZSM-5 on a dry grid with different temperature treatments, we find that the sample boiled to 250°C is more stable under the electron beam. The instability of zeolites under the electron beam is generally attributed to either the presence of trapped water in the pores, or unstable cations in the structure, but this has not been proven before. It is an open question since the first *Nature* publication in 1980. With our new liquid stage capability, we have established this year for zeolites, and we will be working to answer this question of damage mechanism by imaging several different temperature treated zeolites in-situ in water.

In FY 2013, we plan to do an unprecedented experiment, which is the desilication of a zeolite, by developing a heating mechanism for the liquid stage and observing it in-situ in the electron microscope. The desilication will be performed in a liquid with a high pH, and will be visible as the formation of small pores that should combine to make large bubbles in the material. We will combine this with 3D and atomic scale imaging for a full understanding of the desilication process.

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

Jian Zhi Hu

> ***We are developing unique in situ nuclear magnetic resonance (NMR) capabilities, to include existing developed techniques, to advance the understanding of complex electro-chemistry ion transport mechanisms and the performance degradation mechanisms in the electrodes, electrolytes of stationary batteries, and Li-ion and Li-air batteries.***

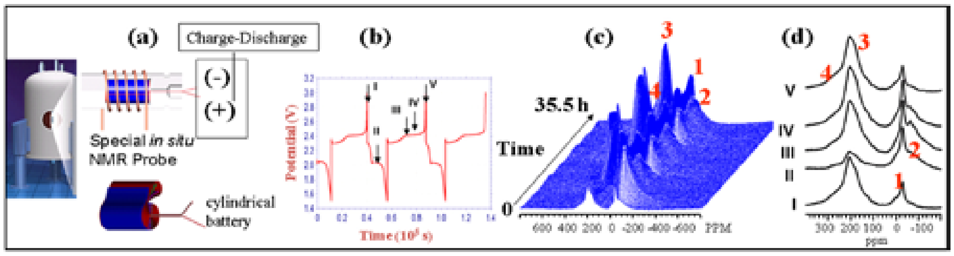
Large-scale stationary energy storage is needed for the widespread use of intermittent renewable energy and for improving the quality of power management in modern electrical grid. For long-term, large-scale applications, the ultimate cost of the storage technology and system should be less than $150/KWh with a lifetime greater than approximately 10–15 years (more than 2000–4000 charge discharge cycles) and 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 are developing 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 and NMR computational and modeling capabilities have been employed to understand the complex chemistry. This combined investigation yields detailed molecular information about ion transport mechanisms and the chemical status of ions both inside electrodes and at the electrode-electrolytes interface. This is especially important for developing new stationary batteries with improved energy and power densities and long-term stability for electrochemical energy storage systems.

Redox flow battery (REB). We performed 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 goal is to understand performance mechanism degradation at elevated temperature. Our findings resulted in six published journal articles. Specifically, our studies offered a molecular level understanding of 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 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* for Li-air batteries and two publications, one in *Journal of Power Sources* and one in *Journal of Physical Chemistry C*, for Li-ion batteries.

***In situ* NMR capability development**. In addition to V-RFB, Li-air, and Li-ion battery research in FY 2012, we developed an *in situ* static NMR capability for investigating live Li-ion/Li-S batteries where either a cylindrical or planar plastic battery can be used. Good results were obtained using a cylindrical Li-S battery as an example (see figure). Our *in situ* NMR cell design is closer to the real commercial battery coin cell design, with the stainless steel container replaced by a plastic holder to allow excitation magnetic field penetrating into battery electrodes and the receiver of the signal generated. The *in situ* NMR capability allows reaction dynamics of the electrochemistry obtained during charge-discharge cycles.



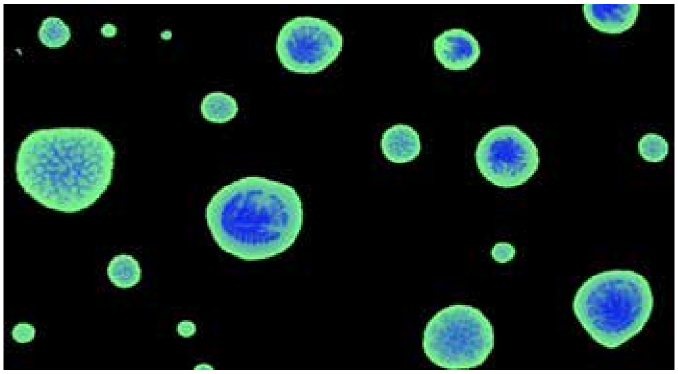
Our in situ NMR capability containing an NMR probe equipped with a CHI-600D for real time charge and discharge of battery during data acquisition; (b) The charge-discharge curve on a Li-S battery; (c) The stacked plot of the *in situ*^{7} Li NMR spectra as a function of time; (d) Highlights the spectra selected from (c) and at the corresponding charge-discharge time points labeled in (b), where the peak assignments are Li from electrolytes and soluble Li-S species (narrow peak1), Li_2S (broad peak 2), a transition Li structure between Li-metal and Li_2S (peak 3), and Li-metal parallel to the magnetic field (shoulder peak 4), respectively.

Chemical Imaging Analysis of Environmental Particles

Alexander Laskin

The production and use of energy often leads to the generation of atmospheric particles that impact a broad range of environmental issues, including atmospheric composition and chemistry, the Earth's radiation balance, polar ozone depletion, and health effects. To address DOE concerns about the safe production and use of energy, we are developing and applying novel experimental approaches to improve our understanding of the origin, fate, and chemical and physical properties of environmental particles.

It is of great interest to understand how the chemical and morphological microstructure of environmental particles affect physicochemical properties such as chemical reactivity, thermodynamics of gas-particle systems, and the 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 multicomponent; therefore, a detailed understanding of their complex chemistry will reduce uncertainties related to their environmental effects. 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.



Color-coded SEM images showing internal structures of mixed NaCl/SOA particles.

This project focuses on developing complementary experimental setups that allow chemical imaging of changes in particle morphology and composition in reactive environments. The research and development efforts are performed along two major directions: first, in the development and application of micro-reactor cells for *in situ* studies of gas-particle reactions using complementary methods of spectro-microscopy; and second, in the development and application of particle depth-profiling methods by single-particle mass spectrometry.

In FY 2011, we evaluated depth-profiling by single particle mass spectrometry, where data indicated that soot particles generated at different temperatures have remarkably different physical and chemical properties. Complementary offline, high-resolution mass spectrometry analysis of soot samples allowed us to provide molecular speciation of aliphatic compounds. For FY 2012, we continued our successful collaboration with Advanced Light Source (ALS) beamline scientists to develop a micro-reaction cell for *in situ* x-ray microscopy studies of gas-particle reactions. We utilized a novel environmental aerosol chamber for experimentally controlled synthesis of internally mixed NaCl/secondary organic aerosol (SOA) and we characterized the composition, shape, and morphology of NaCl/SOA particles, studying their hygroscopic transformations using micro-reaction cell and spectro-microscopy techniques as well as *in situ* single-particle mass spectrometry. We also designed and constructed a new vacuum ultraviolet (VUV) ionization module for advanced depth-profiling of particles with a single-particle mass spectrometer. We conducted 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.

In FY 2013, we will apply complementary chemical imaging techniques in the following laboratory studies: 1) NaCl/SOA and mineral dust/SOA particle chemistry; 2) chemical imaging analysis of iron solubilization processes; 3) fresh soot particles and soot particles aged in atmospheric-like environment; and 4) soot and SOA with an emphasis on evaporation kinetics of semi-volatile compounds. Additionally, we will continue development and modification of the micro-reaction cells for temperature-controlled experiments, and we will will apply VUV depth-profiling approach to mixed organic/inorganic model system with different morphologies.

PN11012/2334

CO_2 Separation Scale-Up

Dale A. King

This project is developing a flexible, modular, mobile CO_2 capture material test capability and evaluating the performance of capture materials from PNNL and other entities relative to conventional baseline materials. The purpose is to develop collaborations with other research facilities to provide a range of scaled testing capabilities to potential CO_2 capture materials.

Currently available technical approaches for CO_2 capture include pressure swing adsorption and capture of CO_2 by liquid adsorbers such as monoethanolamine (MEA). These technologies for CO_2 capture operate near ambient temperature, are costly, and require substantial swings in temperature and pressure. The high cost results from two key factors: low mass fluxes in the separation units and high energy consumption during regeneration of the separation agent. For non-pressure swing adsorption approaches, the separation agent (notably MEA) cost, its operating life and selectivity, and the process complexity are important factors in making any process economically attractive. New technologies that 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 shift reactors can improve the economic viability of coal-based electricity and fuels in the United States.

A drawback of developing new, cost-effective means of CO_2 capture from fossil fuel sources is 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. For post-combustion capture, which is currently the highest priority, MEA can be used as a baseline technology against which other liquid phase CO_2 capture technologies will be compared. For solid adsorbents, the performance baseline standard is zeolite 13x.

The CO_2 capture test capability developed under this project in 2010 consisted of three primary test systems: a wetted-wall column, continuous-scale solid sorbent test cart, and continuous-scale liquid solvent test cart. 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. 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.

Early in the development and selection of liquid solvents, more fundamental material parameters such as reaction kinetics and CO_2 loading capacities were 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 well-controlled interface area between the solvent and 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 to characterize potassium carbonate with mobilized enzymes. In FY 2012, the wetted-wall column was used to collect kinetic data on the PNNL-developed CO_2BOLs in a teaming arrangement with Fluor. This work was funded by DOE's Office of Fossil Energy and was acquired as a result of the wetted-wall column and continuous-scale liquid solvent test cart capabilities.

The continuous-scale solid test cart consists of two columns 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 bed outlet to enable characterization of loading profile and breakthrough characteristics. The beds can be regenerated using thermal swing or pressure/vacuum swing approaches or a combination of the two. The solid cart can operate with a feed flow of between 5 and 20 slpm using two beds of 1.5 L each, with thermal swing adsorption performed between ambient and 200°C and the pressure/vacuum swing adsorption between 0.012 and 4.8 bar. 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. The solid cart

PN10010/2252

was completed in FY 2010. It was then used in 2011 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 in multiple campaigns both in the Sigma V carbon capture laboratory with simulated flue gas and at the flue gas testing facility at the PGE coal plant in Boardman, OR with actual flue gas.

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 and moisture from the CO_2 stream prior to exhaust. The solvent cart can operate with a feed flow of between 5 and 20 slpm using 2 liters of solvent. The solvent flow rate is varied between 50 mL/min and 200 mL/min, and the columns contained 3.2 cm-diameter Sulzer EX packing with a maximum packing length of 83 cm in each column. 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 completed in FY 2011.

Our project modified the solvent cart to a flow-through configuration to measure specific reboiler duty for a CO_2-loaded potassium carbonate solution. We measured reboiler duties at 0.5, 1, and 2 bar pressures and 75% CO_2 loading. The reboiler temperature was varied and a range of lean loadings were produced. Before testing could be performed, this project improved the capability of the solvent cart, including improved flow measurement and control for the reboiler oil loop, the addition of three sample locations axially along the stripper to collect samples and measure gas flow, improved column liquid level sensing to prevent flooding, and the ability to operate the column at sub-atmospheric conditions. In addition, issues related to pumping the high temperature stripper product were addressed with the purchase of a new, high temperature pump.

Following testing, the system was updated to improve solid and solvent off-site testing capabilities. Of particular concern was the need to prevent moisture from condensing in the lines. Minor flue gas constituents such as SO_2, H_2S, and Hg dissolve in the liquid water rather than staying in the gas phase to interact with the CO_2 sorbent material. To address this concern, heated flex lines, a compressor with capability of internal heating, and high temperature flowmeters capable of heat tracing were purchased and assembled on a new “off-site testing” cart.

In addition to the cart testing and upgrades, considerable work was performed to develop collaborations that would position PNNL for future CO_2 capture opportunities. Meetings were held with the National Carbon Capture Center (NCCC) and plans made to allow the solvent cart to be shipped to their testing facility and evaluate it with their flue gas. The PNNL test cart would provide an early TRL evaluation tool at a much smaller scale to augment their larger scale capability and fill their gap between laboratory testing and large pilot scale. This collaboration progressed but was ultimately postponed due to unresolved contractual differences. However, a collaborative relationship was developed between PNNL and the Energy and Environmental Research Center (EERC), affiliated with the University of North Dakota with a coal combustion facility and pilot scale CO_2 capture capabilities for both solvents and sorbents. EERC can benefit from the thermodynamic and kinetic capabilities developed as part of this project; in turn, PNNL can benefit from EERC’s larger-scale testing. EERC worked with GreenCentre Canada to ship PNNL solvents for testing using the wetted wall column and PTX cell. These solvents have not been developed sufficiently to warrant the larger-scale testing available at EERC. These tests are underway, and results are pending.

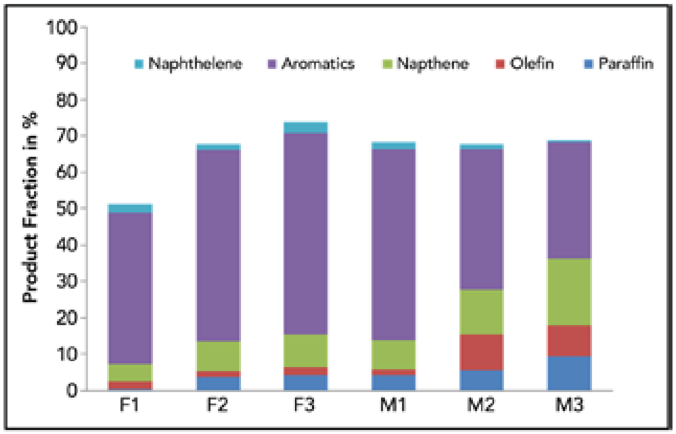
In addition to EERC and NCCC, PNNL has collaborated with Aspen Aerogels (AA) in testing the hydrophobic aerogel materials that AA has developed. PNNL agreed to measure single gas species isotherms and thermal conductivity for two candidate materials that they have developed. AA and PNNL will team to prepare a journal article from the results of these analyses, which should provide an unbiased analysis of the AA materials and publicity to PNNL to showcase capabilities to the carbon capture community. These tests are also underway, with the results pending.

Conversion of Biomass to Jet Fuels

Karthikeyan K. Ramasamy

> ***We seek to understand the catalytic conversion of bioethanol to jet fuel range hydrocarbons, utilizing the fundamental knowledge generated to design 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. With a high interest level in renewable fuel resources, Honeywell is developing a process to produce jet fuel from natural oil and algae resources. Jet fuel requires ~40 wt% of aromatic and cyclic content, along with ~60 wt% of C8 to C16 paraffinic (straight and branched) hydrocarbon due to stringent specifications such as low freezing point, high flash point, and high volumetric density. In addition to unfavorable cost, the above mentioned oil and algae processes produce only the paraffinic content of jet fuel and relies on other resources for its aromatic content.



Comparison of organic product fraction greater than the carbon number C8 between the catalysts tested.

We are studying 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 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 converting 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 primary reaction mechanisms to achieve high jet fuel fraction with 100 percent carbon efficiency. Results showed that ~50 % of the carbon present in ethanol goes toward jet fuel range fraction, with the remaining carbon in the gasoline range fraction and light hydrocarbon gases. At optimized conditions, over 60 wt% of carbon in ethanol ends up in the carbon chain length > C8 (jet fuel range) dominated by aromatic and naphthalene (unsaturated cyclic) compounds.

During FY 2012, our focus was to improve the paraffin and olefin (straight chain) selectivity and reduce unsaturated cyclic compounds such as aromatics and naphthalenes generated from ethanol to fit into the jet fuel composition. From earlier experiments, we identified product distribution changes from high aromatic content in the beginning of the catalyst life compared to higher in straight chain compounds in the later stage of the catalyst life. From these results, two hypothesis were developed to understand the phenomenon. The first hypothesis was based on the pore mouth size modification due to carbon deposition along the catalyst life, which selectively allows only the straight, lightly branched compounds that can fit through the modified pore. To prove this theory, the zeolite catalyst was treated with silylating agent such as tetraethyl orthosilicate (TEOS), as the kinetic diameter of this silylating agent (~0.96nm) is substantially larger compared to the zeolite catalyst pore diameter (~0.55nm). TEOS was expected to deposit on the outer layer of the catalyst and modify the pore size opening. However, results showed that the TEOS was cracked on the external acid sites, and fragmented compounds reacted with the internal acid sites and deactivated the catalysts, which made this approach unsuitable for probing the phenomenon explained earlier.

Our second approach was based on the hypothesis that modifying the catalyst bed length and mixing the catalyst with inert zeolite material (silicalite) the moving bed phenomenon can be replicated. The figure shows the comparison of organic liquid product fraction greater than carbon chain length C8 generated from the commercially acquired fresh catalyst (F1, F2, and F3) and modified catalysts (M1, M2, and M3). These experiments were conducted at 360°C and 300 psig with WHSV between 4.7 and 7.9 h^{-1}. Clearly, there is increased paraffin and olefin content when compared to the respective fresh, modified catalyst. From this research, we are one step closer to achieve renewable jet fuel from ethanol and ultimately from the biomass resources.

PN11014/2336

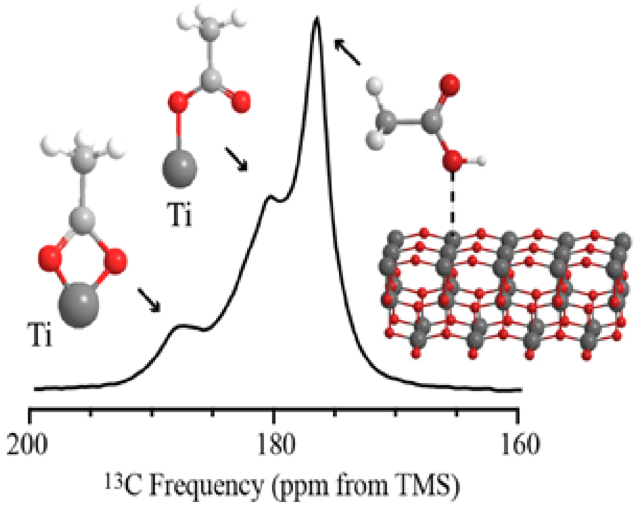
Development and Deployment of Reactive Surface Area Measurement Capabilities Using Nuclear Magnetic Resonance Spectroscopy

Karl T. Mueller

A molecular-level understanding of the specificity, speed, and energetics of solid material surface reactions opens new possibilities for energy production control, pollution mitigation, and a fundamental process understanding that can be harnessed to produce chemicals more efficiently in cost and energy.

The surfaces of solid materials are primary reaction sites for a wide range of important chemical processes, whether these surfaces are found in the environment or exploited for advanced industrial applications. Previously, reaction rates have been measured and mechanisms predicted for a wide range of important chemical processes, but reactions at surfaces are especially difficult to characterize at the molecular level when the systems are either heterogeneous or when they occur in natural environments such as soils or sediments.

The objective of this project is to deploy a range of new experimental tools for measuring reactive sites and reaction rates on the surfaces of materials. We are using solid-state nuclear magnetic resonance (NMR) spectroscopy to probe surfaces and molecules adsorbed to these surfaces. Solid-state NMR is an isotopically selective tool that provides information on local electronic and magnetic environments of NMR-active detected isotopes. For spin-1/2 nuclei such as ^{13}C, the primary information comes from measurements of unique species via the isotropic chemical shift. The results of this research will provide a clearer understanding of chemical reactivity at complex surfaces by describing the sites on the surface that are reactive and what the structures of reactive molecules are when they are found at surfaces. By acquiring data at different temperatures, we are also able to describe the energetics of formation and removal of these reactive species.



Solid-state ^{1}H/^{13}C CPMAS NMR offers a superior characterization of the adsorption of 1-^{13}C acetic acid to the surface of anatase. Multiple binding sites are clearly resolved in the one-dimensional NMR spectrum, and our assignments are illustrated with molecular models.

In the past year, we built and deployed a set of dosing stations to load NMR-active probe molecules onto surfaces for analysis utilizing the NMR instrumentation at EMSL. Two gas-phase dosing stations and an *in situ* loading cart were developed for this work, which allowed adsorption of ^{13}C-enriched ethanol and acetic acid as probes of surface sites. The probe molecules were labeled at molecular positions that correspond to the carbons that are part of the alcohol and acid groups, respectively, allowing for facile ^{13}C NMR studies of bonding environments.

Primary experiments focused on ^{1}H/^{13}C cross-polarization magic-angle spinning (CPMAS) NMR measurements and were carried out at magnetic fields of 14.1 T, 17.6 T, and 20.0 T corresponding to ^{1}H resonance frequencies of 600, 750, and 850 MHz, respectively. At these high magnetic field strengths, spectra were accumulated with superior signal-to-noise ratios and sensitivity, and maximal spectral resolution was achieved.

Results were obtained detailing the bonding environments of the probe molecules ethanol and acetic acid on polycrystalline alumina (the gamma phase) and titanium dioxide (the anatase phase). In particular, the range of binding sites for acetic acid on anatase was investigated. One- and two-dimensional NMR spectra demonstrated the resolution possible at very high magnetic field strengths and up to three, possibly four unique binding sited have been identified. By stretching the ^{13}C spectrum into a second spectral dimension, connectivities of the carbon atoms to unique ^{1}H environments have been established. Additional studies included the temperature dependence and pre-dosing processing conditions for the adsorption of ethanol on the surface of a γ-alumina sample. In this instance, primarily physisorbed species were detected, and it appears that the chemical shift range for ethanol on aluminas may be too small to detect differences between physisorbed and chemisorbed species.

Overall, the discovery of multiple binding sites as well as the experimental protocols for detecting these sites via solid-state NMR have added greatly to our knowledge of reactive surface structures on complex materials such as titania.

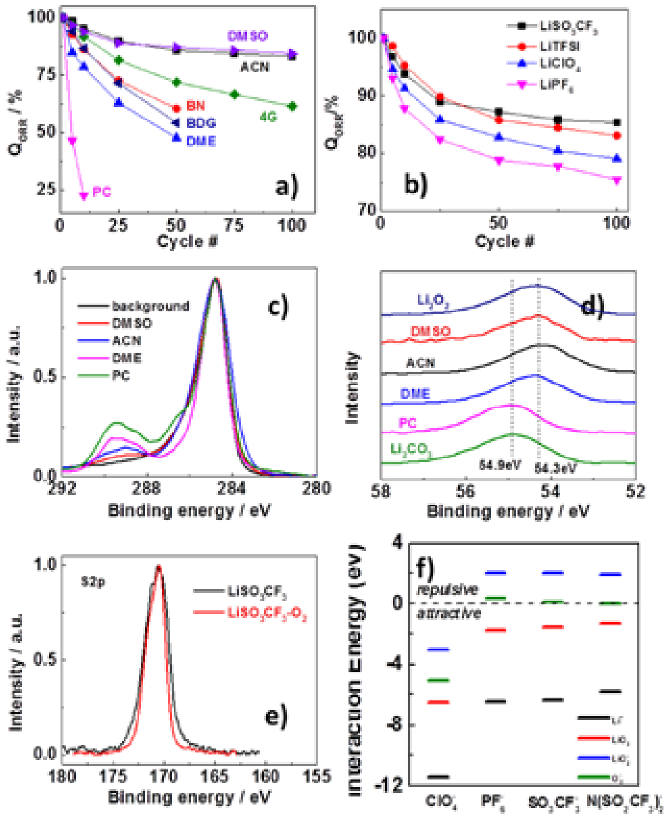
PN12020/2421

Development of Bifunctional Electrocatalysts for Rechargeable Lithium-Air Batteries

Yuyan Shao

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. Advanced bifunctional electrocatalysts for oxygen reduction and oxygen evolution in air electrodes are needed. In order to do this, nonaqueous electrolytes that are stable in oxygen-rich electrochemical conditions are critical.



a)-b) Cycling stability of solvents and Li salts; c)-e) XPS of cycled electrodes in different electrolyte; f) DFT calculations on the stability of Li salts.

The research under this project is providing a fundamental understanding of electrode reaction mechanisms and high-performance electrolytes/electrodes 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 the design and development of electrocatalysts materials and stable electrolytes.

In FY 2012, we further optimized the new technology platform for mechanism study and electrocatalyst/electrolyte development. This new platform simplifies the study of oxygen reaction mechanism in simulated Li-air conditions. The platform also significantly accelerates the screening of electrocatalysts and electrolytes: the test time of one is a few hours compared with days or weeks in traditional test methods. We focused on stable electrolytes study, including nonaqueous solvents and Li salts. A stable electrolyte is critical for both oxygen reaction mechanism study and electrocatalyst development because this work needs to be done in electrolyte, one of the three key components (anode, cathode, electrolyte) of a battery that is, therefore, important for practical Li-air battery development.

We have learned that for nonaqueous solvents 1) alkyl carbonate-based electrolyte are usually unstable, among which linear carbonates are slightly more stable than cyclic carbonates; 2) like various glyme, ether-based electrolytes are more stable than carbonates; 3) nitrile-based electrolytes are even more stable than carbonates and ethers; and 4) acetonitrile and DMSO are the most stable. For Li salts, Li triflate ($LiSO_3CF_3$) and Li Bis(Trifluoromethane-sulfonyl) Imide (LITFSI) are the most stable, followed by Li perchlorate ($LiClO_4$) and Li hexafluorophosphate ($LiPF_6$). The surface chemistry study and density functional theory (DFT) calculations were carried to illuminate mechanisms behind the stability trend.

This project leads to a research platform and identify stable electrolytes for rechargeable Li-air battery research, which is the most critical issue in the community.

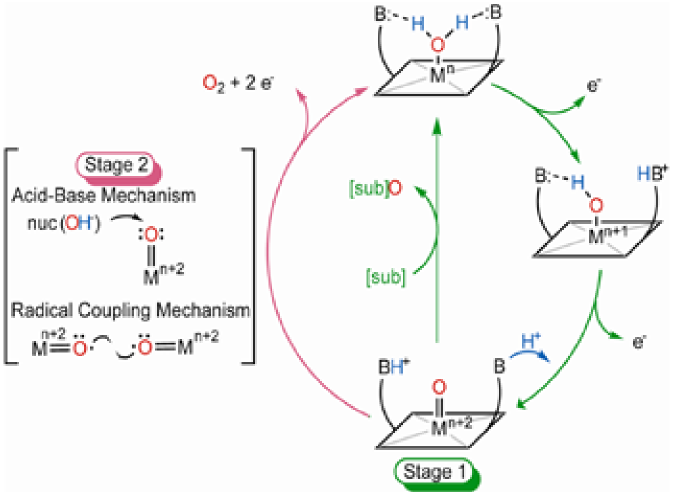
Development of Inorganic Water Oxidation Electrocatalysts

Aaron M. Appel

This project will develop new classes of homogeneous inorganic water oxidation electrocatalysts that improve on 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 and incorporate the essential features of natural systems into synthetic systems. To avoid high or low energy intermediates in the catalytic cycle, we seek to utilize effective proton management and to match the energetics of catalytic intermediates to approach thermodynamic equilibrium for each step. 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.



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-oxygen bond formation with the reactive metal oxos.

We attack the challenging four-electron process to oxidize water by studying the catalytic cycle in two stages. 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.

In 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 did not appear to be active for water oxidation. However, the reverse reaction (oxygen reduction) explored by our University of Washington collaborators is an active electrocatalyst that demonstrates high selectivity to the reduction of O_2 to water. The second ligand system studied in FY 2011 explored the use of five-coordinate pyridine ligands (Py5). The complexes $[(Py5)M(H_2O)]^{2+}$ and $[(Py5)M(OH)]^{2+}$ (M= Fe, Co) led to a rare example of an Fe^{III}—OH complex. The proton-coupled electron transfer from the aquo complex oxidation and thermo-chemical properties were studied, which led to the following year's research direction.

In FY 2012, our efforts focused on incorporating proton relays into the second coordination sphere of four-coordinate Fe^{II} aminopyridine complexes. Recently, a family of complexes that shared a *cis*-$[Fe(N_4)X_2]$ (X = Cl or Br) formulation was reported to catalytically oxidize water to O_2. The synthetic possibilities for modification of the ligand environment to incorporate hydrogen bonding groups were well-established, so we set out to examine the structures and catalytic water oxidation behavior of a series of novel Fe^{II} complexes. These complexes are indeed water oxidation catalysts, with initial rates higher than the corresponding complexes which lack the proton relays. The study of these complexes has identified promising features for the design of new catalysts, as submitted for publication and presented at two technical conferences.

The results of this project will influence the design of additional catalysts, has resulted in interactions with currently funded projects, and will be included in other proposals. Future work should focus on complexes that contain a pK_a matched proton relay that will work with chemical oxidants or directly as electrocatalysts.

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

Julia Laskin

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 the characterization of microbial biofilms. We are using *Shewanella oneidensis* and cyanobacteria biofilms as a model systems for obtaining molecular level understanding of metal reduction and CO_2 sequestration by microbial communities.

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. *Synechococcus* sp. PCC7002 is a photosynthetic bacterium that in the presence of light converts CO_2 into sugars and other organic molecules. During the course of this project, we have developed approaches for comprehensive MS characterization of extracellular material in biofilms. These tools have been used for the detailed characterization of chemical gradients generated at interfaces between biofilms and mineral surfaces or interfaces between different microbial communities grown on agar plates.

MS imaging experiments of chemical gradients generated at interfaces revealed the identity of several 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 two novel platforms for imaging biological samples. The first platform utilizes ambient 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. We demonstrated highly sensitive ambient nanoDESI imaging with spatial resolution > 10 µm, 10× better than that obtained using more traditional ambient pressure surface ionization techniques. The second system combines the C_{60} secondary ion mass spectrometry (SIMS) system with a high resolution Fourier transform ion cyclotron resonance (FT-ICR) MS imaging apparatus. The one-of-a-kind C_{60} SIMS FT-ICR MS apparatus is characterized by high mass accuracy (< 1 ppm), high mass resolving power ($m/\Delta m_{50\%} > 200{,}000$), and tandem MS capabilities. The ability to resolve isobaric peaks in SIMS of biological samples is key to characterizing chemical gradients present in such complex systems. Recent instrumental upgrades drastically improved platform performance; specifically, the simplification of ion transfer optics significantly increased sensitivity and mass range-enabling detection of intact lipid species with good sensitivity.

In FY 2012, we have 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. Spatial profiling of chemical signals generated by microbial communities in response to their environment is essential for detailed understanding of interactions between different microbial communities and between biofilms and mineral surfaces. These novel experimental tools were combined with unique molecular networking bioinformatics tools developed by our colleagues at the University of California, San Diego. Facile detection of metabolites from living microbial communities using nanoDESI and efficient classification of metabolites based on the MS/MS data presents a unique new tool for studying metabolic exchange between microbial communities.

Future research will involve multimodal characterization of *Shewanella* and *Synechococcus* biofilms, providing unique insights on molecules responsible for electron transfer to mineral surfaces and on biological sequestration of carbon dioxide.

PN11028/2350

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

Grant E. Johnson

This project will employ soft landing of mass-selected ions and characterization with* in situ *techniques to prepare precisely-defined catalytic materials and to establish structure-reactivity relationships that will enable the rational design of improved catalysts.

The size, structure, charge state, and composition of nanoparticles, clusters, and complex molecules supported on surfaces significantly impacts their chemical and physical properties. The existing approach for preparing metal nanoparticles and clusters involves the reduction of metal precursors in solutions containing organic capping ligands. While this method may produce nanoparticles with controlled size distributions and morphologies, it is unable to access the subnanometer size regime with truly monodisperse "atom-by-atom" precision. Soft landing of mass-selected ions is a powerful approach for the preparation and modification of surfaces and enables unprecedented control over the composition of the deposited materials. For instance, through soft landing of mass-selected ions, metal clusters with specific sizes (8–10 atoms) exhibited pronounced catalytic activity toward reactions such as the oxidation of CO to CO_2 and the dehydrogenation of propane. Further, electrospray ionization of molecular precursors enables the production of high intensities of catalytically active clusters for subsequent soft landing onto substrates. In addition, physical synthesis techniques such as laser vaporization and magnetron sputtering combined with gas aggregation may prepare unique materials that cannot be synthesized using traditional approaches.

The size and charge state of 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 were shown to retain their charge when deposited onto fluorinated monolayers. In contrast, partial and complete neutralization of charge was observed when the same clusters were 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 metal clusters on surfaces and are the subject of a publication in *ACS Nano*.

Characterization of size-dependent properties of nanoparticles and clusters relies on the availability of clean homogeneous samples for analysis by transmission electron microscopy (TEM). Atomically monodisperse gold clusters containing exactly 11 gold atoms 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 TEM sample preparation, as it may be extended easily to other materials. These results are the subject of a publication in *Analytical Chemistry*.

A new position-sensitive detector referred to as IonCCD™ has been examined using different charged particles. It is a modified light-sensitive charge-coupled device (CCD) engineered for direct charged-particle detection. Combining the IonCCD™ with a double-focusing sector field mass spectrometer, we demonstrate fast data acquisition. Detection of hyperthermal biomolecular ions produced using an electrospray ionization source is also presented. In addition, we demonstrate the possibility of simultaneous separation and micro-array deposition of material using a miniature MH-MS. This work was published in and featured on a cover of the *Journal of the American Society for Mass Spectrometry*.

The IonCCD™ was employed to characterize the ion optics and ion beam focusing in a custom built mass spectrometer designed for soft and reactive landing of mass-selected ions onto surfaces. The IonCCD™ was placed at several stages along the path of the ion beam to determine the focusing capabilities of the various ion optics, which include an electrodynamic ion funnel, two radiofrequency (rf)-only collision quadrupoles, a mass resolving quadrupole, quadrupole bender, and two einzel lens assemblies. Combined with SIMION simulations, we demonstrated that the IonCCD™ can identify minor errors in the alignment of charged-particle optics that result in erratic trajectories and significant deflections of the ion beam. This information may be used to facilitate the design, assembly, and maintenance of custom-built mass spectrometry instrumentation used for soft landing of mass selected ions. These results were published in the *Journal of the American Society for Mass Spectrometry*.

Continuing areas of inquiry will include the following: 1) preparation of atomically monodisperse nanoparticles and clusters on surfaces and examination of their size and shape-dependent reactivity; 2) investigation of the charge retention and neutralization behavior of multiply charged anionic polyoxometalate clusters deposited onto surfaces; and 3) structural and thermodynamic characterization of subnanometer gold clusters in the gas phase.

PN10026/2268

Environmental Chamber Studies of the Interactions of Anthropogenic and Biogenic VOCs

John E. Shilling

Accurately representing the effect of organic particles, which are a large fraction of all aerosol particles, on climate remains a challenge for atmospheric models. The focus of this project is to improve the scientific understanding of the organic aerosol particle lifecycle using laboratory experiments and detailed process modeling.

Measurements show that organic aerosol particles comprise 20 to 90% of the total atmospheric aerosol mass. However, atmospheric models have difficulty in reproducing the properties and concentrations of organic particles observed in the atmosphere. Recent field measurements have elucidated two important gaps in model representations of the organic particle lifecycle. First, organic particle formation from biogenic compounds appears to be enhanced in the presence of anthropogenic emissions by some unknown mechanism, implying a climatically significant anthropogenic radiative forcing mechanism that is not currently captured in models. Second, observations have suggested that organic particles are solids or semi-solids rather than liquids as currently assumed in most models. Accurate reproduction of these properties in models has important consequences for reducing the uncertainties associated with the effect of aerosol on climate forcing.

This project focused on coupled laboratory experiments and modeling studies aimed at improving the scientific understanding of the organic particle lifecycle, particularly in regards to the aforementioned field observations. The work described is aimed at testing the hypotheses that organic particle formation from biogenic gases is altered in the presence of anthropogenic gases, and that organic particles exist as semi-solids and therefore evaporate slowly and do not serve as a solvent for further organic particle condensation. We generated organic particles under controlled conditions in a continuous-flow environmental chamber and measured their size and chemical composition in real time. We then attempted to reproduce experimental data using a detailed process model while varying model assumption. Insights gained from the application of the process model to chamber data will lead to a more accurate representation of organic particle lifecycle in larger-scale models. The ultimate goal of this research strategy is to improve the accuracy of climate forcing in these larger-scale models.

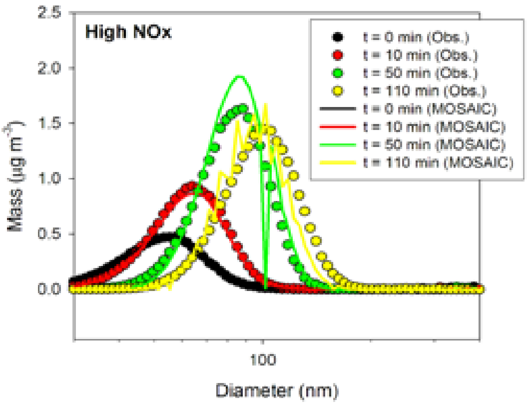
In the first series of experiments, we studied the evaporation of organic aerosol particles generated from the ozonolysis of α-pinene, a biogenic emission. Particles were produced by oxidizing α-pinene with 300 ppbv ozone in one side of the chamber. After the reaction, the particles and resultant gases were transferred to the second side of the chamber, where they are diluted with pure air to initiate evaporation. Particle size and chemical composition is measured in real time with a scanning mobility particle sizer (SMPS) and a high-resolution mass spectrometer (AMS), respectively. The effects of several different experimental variables on the particle evaporation rate were explored. Particles were continuously generated under dry conditions (RH < 2%) in the production chamber and transferred continuously to the dilution chamber through either a plain stainless steel line or a 15 L reservoir filled with activated carbon. In these experiments, we varied the aerosol dilution ratio 5–15, loading 12–150 $\mu g/m^3$, and residence time in the dilution side of the chamber 3–5 h. Regardless of conditions, we observed no measurable aerosol particle evaporation. To investigate evaporation over longer time scales, we performed experiments in which aerosol in the production chamber was rapidly transferred in a single batch to the dilution chamber. The dilution ratio in these experiments was 7:1, and particle size distributions were monitored in real time up to 24 h. In these experiments, we observe slow evaporation of ~20% of the aerosol mass over the course of the experiments. Together, results confirm that organic aerosol particles may exist in the semi-solid state and evaporate more slowly than would be predicted from traditional atmospheric models.

In the second series of experiments, we collaborated with the Georgia Institute of Technology to measure the volatility and yield of organic aerosol particles formed from the photooxidation of isoprene in the presence of different NO_x concentrations. Isoprene is the most abundant non-methane biogenic emission, so even small perturbations in particle yield and volatility by NO_x (an anthropogenic emission) may have an effect on local and global organic aerosol production. Particles were generated in our chamber at different NO_x concentrations at low RH (< 5%) and passed through a thermodenuder at different temperatures to investigate particle volatility. H_2O_2 and HONO were used as OH precursor for low-NO_x and high-NO_x experiments, respectively. The yields demonstrate a complex dependence on NO_x concentration that we are still analyzing. In general, the volatility of organic particles decreases after peak aerosol growth, indicating that the formation of highly oxidized, low-volatility species increased as the particles were photochemical aged. However, it is found that aerosol formed under low-NO_x conditions is more volatile. Results show that ~60% of low-NO_x isoprene organic particle mass evaporated in the thermodenuder at 100°C compared to < 40% evaporation of particles produced under high NO_x conditions. Further, under high-NO_x conditions, 10% of aerosol mass remains even at 200°C, compared to full evaporation of low-NO_x particles, suggesting that species with low volatility are formed when isoprene is oxidized under high-NO_x conditions. Our results show that

PN12027/2428

aerosol produced from mixtures of biogenic and anthropogenic emissions may be transported over longer distances in the atmosphere than aerosol produced in the absence of anthropogenic emissions. These results will be presented at the American Geophysical Union fall meeting and are being prepared for publication.

To reproduce the full aerosol lifecycle, both evaporation and growth of particles must be studied. To understand the organic particle growth mechanism, data from the chamber studies were interpreted with the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), a comprehensive aerosol box model developed at PNNL. Organic particles were generated either from the ozonolysis of α-pinene or the photooxidation of isoprene in the presence of NO_x (see the preceding paragraphs for experimental details). Particle size distributions and mass loadings were measured in real-time using the SMPS. Organic particle formation in MOSAIC was parameterized using 4-bin volatility basis set (VBS) fits of the time-dependent SMPS data. Gas-particle mass transfer of these four organic species was performed dynamically to size-distributed aerosols, as opposed to bulk equilibrium treatment used in previous modeling studies. Thus, in addition to simulating the organic particle mass formed, MOSAIC also simulated the evolution of aerosol size distribution during particle growth. This added feature can be used to probe the underlying mechanism(s) of organic particle formation such as reactive uptake vs. absorptive partitioning. In the reactive uptake formation mechanism, the condensing organic vapors are assumed to be effectively nonvolatile (i.e., they are assumed to instantaneously react upon condensing, so that their vapor pressures are essentially zero), in which case the growth of particles would be controlled by aerosol surface area. In contrast, an absorptive gas-particle partitioning mechanism based on Raoult's law assumes that condensing organic vapors are absorbed into the pre-existing organic aerosol mass while maintaining non-zero partial pressures over the particles after absorption. In this case, the growth of particles would be controlled primarily by aerosol volume. The time-dependent evolution of the size distributions resulting from reactive uptake and absorptive partitioning may be quite different depending on the actual vapor pressures of the condensing species, pre-existing aerosol size distribution and composition. In general, reactive uptake tends to narrow the size distribution while absorptive partitioning tends to broaden the size distribution. Model analysis of the chamber data for the isoprene experiments showed that the observed evolution of size distribution resembled that produced from a reactive uptake mechanism in the early stages of growth while gradually shifting to an absorptive-partitioning type mechanism in the latter stages. These results are still preliminary and need to be fully analyzed before reaching final conclusions. Nevertheless, we developed a unique measurement-modeling strategy that can be applied in the future under programmatic funding to probe organic aerosol formation mechanisms in a novel fashion.



Example of comparison of observed and modeled (reactive uptake) size distributions at increasing reaction times. Excellent agreement at 50-min interval suggests reactive uptake mechanism is sufficient to explain the growth, but broadening in the observed size distribution compared to model at 110-min interval suggests that absorptive mechanism has begun to play a role.

Finally, in another series of experiments, we generated particles in the chamber, collected them of Teflon filters, and sent the particle-laden filters to University of British Columbia (UCB) and University of California, San Diego (UCSD) collaborators for analysis. Two types of particles were generated. First, we generated particles from the photooxidation 1,2,4-trimethylbenzene under low NO_x conditions in the continuous-flow chamber. 1,2,4-trimethylbenzene was injected into 24 sLpm of pure air flow to produce concentrations of 4.8 ppmv in the chamber prior to reaction. An additional 1 sLpm flow of pure air was bubbled through a 50% solution of hydrogen peroxide in water and added to the chamber. Photooxidation was initiated by turning on 105 UV (Q-labs UVA-340) lights surrounding the chamber, which generate OH radicals from hydrogen peroxide photolysis. The resultant particles were collected on filters and sent to UCB, where they were extracted with water, combined with ammonium sulphate, and analyzed using optical and fluorescence microscopy. As particle humidity increases, we observe the particles separate into two non-crystalline phases in particles, one organic rich phase and one aqueous phase. These results reveal that atmospheric particles can undergo liquid-liquid phase separations that will affect the gas-particle partitioning of atmospheric semi-volatile organic compounds, the scattering and absorption of solar radiation, and the uptake of reactive gas species on atmospheric all of which have important implications for climate predictions. These results were published in the *Proceedings of the National Academy of Sciences*.

We generated particles from the photooxidation 1,2,4-trimethylbenzene under high-NO_x conditions using similar methods. However, in these experiments, OH was generated from HONO photolysis rather than hydrogen peroxide, producing particles that have different chemical composition. Particles were collected silicon nitride windows and sent to UCSD collaborators who performed organic functional group analysis by scanning transmission x-ray microscopy with near edge x-ray absorption fine structure (STXM-NEXAFS) spectroscopy. Analysis showed high concentrations of carboxylic carbonyl, alkyl, and hydroxyl groups in the non-spherical particles, implying that they were liquid when impacted on the window. These laboratory-generated particles had similar spectral features with those collected in field measurement campaigns in Bakersfield, CA; Whistler, BC; the Scripps Pier, CA; Mexico City; and Chile. These results have been submitted for publication to *Aerosol Science and Technology*.

Exploitation of Kinetic Processes in Gas Separations

Richard M. Williams

We are investigating kinetic-based gas separations processes for use in national security applications such as nuclear explosion monitoring. A successful outcome of this project is the identification of sorbents and gas separation techniques that require less energy and fewer consumables compared to the methods currently used.

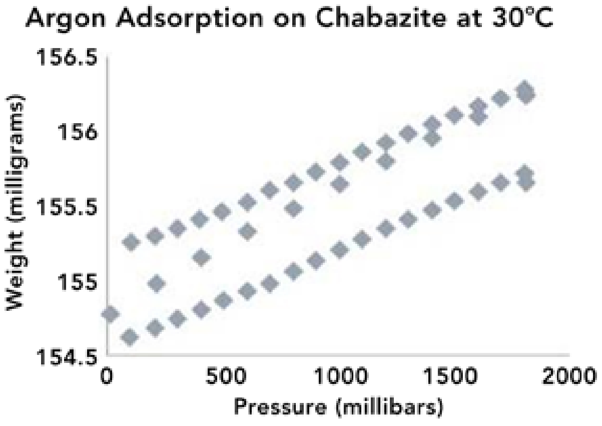
There is a need to develop more efficient, less energy intensive techniques for separating and concentrating trace gases from the atmosphere. Current techniques, including the use of liquid nitrogen cooled or large ambient temperature traps, rely on the equilibrium properties of the adsorption process and are energy intensive due to the use of cryogens or the need to heat large amounts of adsorbent. Separation techniques that exploit the kinetics of the adsorption process have potential to reduce equipment size, energy requirements, and remove the need for consumables such as liquid nitrogen. Equilibrium data for some adsorbents can be found in the literature. With the exception of limited data relevant to oxygen-nitrogen separations, however, kinetic data are generally not available.

Kinetic separations techniques (e.g., rapid-pressure-swing-adsorption or R-PSA) are rapidly gaining acceptance for application-specific gas separation needs for new adsorbent materials developed specifically with kinetic properties in mind. Kinetic-based gas separations allow for the use of smaller adsorption beds because they rely more on timing and less on capacity; therefore, future systems can be much smaller than current designs. Additionally, R-PSA schemes operate at ambient temperatures (no external cooling requirements), further benefiting field deployable systems. This project combines novel finite-element simulations with experiments to advance concepts for next-generation whole air collection and purification systems. New advanced simulation methods will be developed that provide a more complete physical picture of the actual separations process.

Initially, we collected data using a hidden dynamic adsorption analyzer and adsorption breakthrough instrument assembled for this project. Data collected included both equilibrium and kinetic parameters for process models using COMSOL multiphysics and Aspen adsorption. These finite element and difference models provide a means to experiment with different separation techniques and ultimately develop promising kinetic adsorption-based separation processes. Specifically, the kinetic and equilibrium properties collected for large number of adsorbent-gas combinations have included N_2, O_2, CO_2, Ar, Kr, Xe, and CH_4. Adsorbents including activated charcoal, Carboxen 1000, Carboxen 569, MS 5A, MS 13X, ETS 10, Ca Chabazite, and MOF 5 have been characterized. A linear driving force approximation has been used to describe adsorption kinetics, and more complex models that include macropore convection and micropore diffusion are being developed using COMSOL multiphysics.

Our process modeling tool preparation has also been accomplished. Ca Chabazite stands out as the material showing the largest kinetic effects and appearing the most promising for argon separation. Data have been valuable in assessing proposed separation techniques. For instance, the single component uptake data for Xe on Chabazite appeared promising. However, a careful examination accounting for competition with N_2 and O_2 indicates that Xe uptake from the atmosphere would be lower than that seen with many carbon-based adsorbents. Milestones have included simulation-based data analysis techniques to extract diffusivities and other kinetic properties and completing an initial measurement campaign of a significant fraction of relevant adsorbent/adsorbate systems using the Hiden adsorption analyzer.

In FY 2013, we will continue to measure promising adsorbents. Based on modeling results, adsorbents will be revisited, and more data collected when required. The focus will shift from data collection to process development. A paper is planned using the Chabazite data and the more complex kinetic process simulation being developed in COMSOL multiphysics. The data and modeling effort will also be used to develop a concept papers for whole air separation. It is envisioned that this will be a rapid cycle pressure swing process related to Ar separation.



Hyden data showing non-equilibrium uptake of Ar due to slow adsorption kinetics.

PN12029/2430

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

Xiao Lin

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.

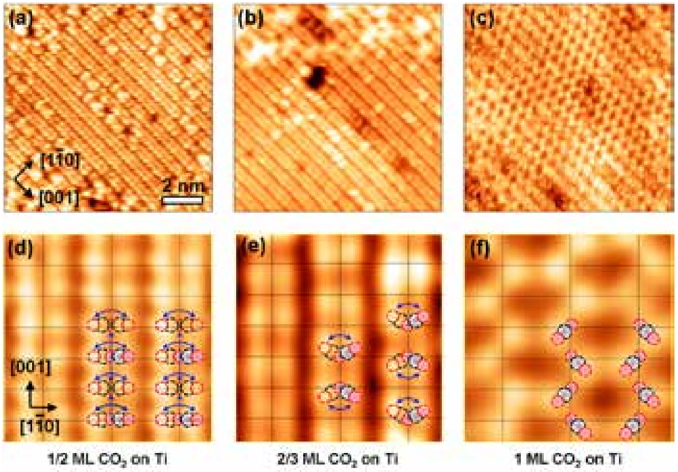
As industries are relying on fossil fuels for energy and the global warming problem mounts, there is an immediate need for improving the fundamental understanding of CO_2 activation, which is instrumental for carbon sequestration and CO_2 conversion to fuels. Using TiO_2(110) and other well-characterized oxides surfaces as the models provides us with an opportunity to understand the fundamental aspects of elemental processes such as CO_2 adsorption, diffusion, and reaction.

In FY 2010 and FY 2011, we studied the adsorption and dissociation of propane-1,3-diol and CO_2 molecules on TiO_2(110) surfaces. In FY 2012, we focused on the CO_2 layer structure on TiO_2 surfaces and CO_2 interaction with the oxygen adatoms on TiO_2 by means of scanning tunneling microscopy, molecular beam techniques, temperature programmed desorption, infrared reflection adsorption spectroscopy, and theoretical calculations by dispersion-corrected density functional theory and *ab initio* molecular dynamics.

Detailed level of understanding about CO_2 adsorption, site specific binding, translational and rotational diffusion dynamics, and desorption kinetics on TiO_2(110) surface have been obtained. Using a combined experiment and theory approach, we obtained a comprehensive understanding of the coverage dependent of CO_2 behavior on rutile TiO_2(110). We found that CO_2 binds through one of the O atoms on top of Ti_{5c} site and is tilted towards one of the neighboring O_b rows. At low coverages, this special configuration provides a low diffusion barrier that proceeds via rotation and tumbling mechanism. At 2/3ML coverage, the CO_2 diffusion is observed to cease. Pairs of CO_2 molecules bound on neighboring Ti_{5c} sites are observed with a free Ti_{5c} site separating the pairs. As the coverage increases to 1 ml, all Ti_{5c} sites become occupied and rotation motion also ceases leading to zigzag arrangement of tilted CO_2 molecules, which is a result of fine balance between attractive quadrupole-quadrupole interactions and steric repulsion. Above 1 ML, CO_2 can bind on O_b rows with a lower desorption energy compared with the Ti_{5c} row, but the amount is limited as 0.5 ML, a result of an out-of-phase zigzag arrangement of CO_2 on neighboring Ti_{5c} rows that, while blocking half of the Ob sites, allows for 0.5 ML adsorption of strongly bound CO_2 on top of Obs. Strong quadrupole-quadrupole interactions were observed between Ti_{5c}-bound CO_2 and O_b-bound CO_2. In conclusion, this combined experimental and theoretical study provides insight into CO_2 binding configurations on surface sites on TiO_2(110), demonstrates their highly dynamic nature, and shows that quadrupole-quadrupole interactions play an important role in determining detailed surface structures at different coverages.

We also studied CO_2 adsorption on TiO_2(110) with pre-dosed oxygen. CO_2 molecules were found to sit preferentially on Ti_{5c} sites next to the oxygen adatoms (O_as) to form CO_2/O_a complexes. Our results show that at 50 K, CO_2 is bound to O_a only *via* weak dispersion forces. Further temperature dependent studies revealed that the CO_2 binding energy next to O_as is about 20 meV smaller than that on V_o's.

Future studies will extend to other oxides, e.g., RuO_2(110), which will be grown epitaxially on the Ru(0001) surface that has the same structure as rutile TiO_2(110) but is metallic and significantly more active. It has been shown to activate CO_2 readily to chemisorbed CO_2 and form negatively charged dimerized species, CO_2-CO_2. Further H_2 can be chemisorbed on Ru-cus sites and dissociate to form two bridging hydroxyl groups. While H transfer from Ru sites to lattice oxygen is observed on bare surfaces, we will explore possibilities of H transfer to chemisorbed CO_2^- leading to C-H bond formation. Comparison of results from different oxides (TiO_2, RuO_2) with identical structural motifs will provide valuable information about structure-activity relationships on such model systems.



STM images from CO_2 overlayers adsorbed on TiO_2(110) without oxygen vacancy at 50 K. Panels (d-f) show high magnification images from (a-c). The images are overlaid with the time average of the configurations sampled by CO_2 during STM imaging. The grid dotted lines correspond with the positions of Ti_{5c} ions.

PN10038/2280

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

John S. Loring

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 ($scCO_2$).

One approach to slow the flux of greenhouse gases into the atmosphere is geologic carbon sequestration (GCS), whereby CO_2 is stored deep underground, such as in saline basalt formations or exhausted oil wells. At targeted injection depths, carbon dioxide exists as a supercritical fluid ($scCO_2$). With repeated injections, the $scCO_2$ will displace formation water, and the pore space adjacent to overlying caprocks will eventually be dominated by dry to water-saturated $scCO_2$. Water-bearing $scCO_2$ is highly reactive and capable of carbonating and hydrating certain minerals, whereas anhydrous $scCO_2$ can dehydrate water-containing minerals. Because these geochemical processes affect solid volume and thus porosity and permeability, they have the potential to affect the long-term integrity of the caprock seal. 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 chief goals of this project are to integrate a powerful suite of *in situ* experimental capabilities recently developed at PNNL to investigate reactions between minerals and $scCO_2$ containing variable amounts of water, and to focus these capabilities on a range of geologically relevant host and caprock materials. These in situ probes include infrared (IR) spectroscopy, magic angle sample spinning nuclear magnetic resonance (NMR) spectroscopy, atomic force microscopy (AFM), and x-ray diffraction (XRD). 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.

While funding for this project arrived mid-year, the work performed for the remainder of FY 2011 set the stage for progress in FY 2012. Our focus during FY 2011 was to complete experiments that were already underway on the olivine forsterite and the serpentine antigorite, and to initiate studies on hydration/dehydration of the expandable clay, montmorillonite. Additionally, chemicals and equipment were purchased using FY 2011 funds in preparation of mineral studies in the last 2 years of the project.

There were three main focuses in FY 2012. The first was to analyze and interpret IR spectroscopic data on forsterite and antigorite carbonation in wet $scCO_2$. These results revealed that minerals exposed to wet $scCO_2$ are covered in thin films of adsorbed water, and these films contain high concentrations of dissolved ions (e.g., as high as 3 M bicarbonate). This work also uncovered an incongruent dissolution mechanism for antigorite, which leads to the formation of high surface area polymerized silicate skeletons that adsorb more water from the $scCO_2$ and hinder metal carbonate precipitation.

The second focus was to initiate and complete an integrated IR, NMR, and XRD carbonation study on the pyroxene-like mineral, wollastonite, exposed to wet $scCO_2$. This detailed research showed that carbonation rates increased with increasing temperature, pressure, water content in the $scCO_2$. Water films were shown to adsorb on high surface area calcite and porous amorphous SiO_2 carbonation products, and an amorphous calcium carbonate intermediate was also detected.

Finally, the third focus of our work during FY 2012 was the hydration/dehydration of the expandable clay, montmorillonite, exposed to wet $scCO_2$. This integrated IR, NMR, and XRD study showed for the first time direct spectroscopic evidence that CO_2 intercalates and expands these clays under geologic reservoir conditions. Results have been accumulated that can be used to predict the interlayer spacing and water content at any $scCO_2$ water saturation concentration for Na-, Ca-, and Mg-saturated Wyoming bentonite (a montmorillonite clay). The spectroscopic results also reveal molecular-scale details about the structure of intercalated CO_2 and water. In summary, the work in FY 2012 resulted in four published articles, two submitted manuscripts, and 11 conference presentations.

In FY 2013, we will continue our integrated capability investigative approach to 1) complete hydration/dehydration studies of montmorillonite clays, which will result in three targeted publications; 2) initiate and complete detailed studies on the dependence of adsorbed water-film thickness on dissolved ion concentrations, focusing on the olivines forsterite and fayalite; and 3) broaden our studies to other relevant minerals to include non-expandable clays, chlorites, feldspars, and/or natural rock samples.

PN11040/2362

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

Albert J. Fahey

This research will lead to a basic understanding of how oxide and elemental ions form on various substrates and under different conditions through elemental oxide measurements and dioxide signals from single particles under prescribed conditions. This 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 the application of method and fundamental mechanisms of sputtering ionization will be obtained and analyzed.

Ratios	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	^{235}U (cps)
R002	0.08967 ± 0.00010	10.40244 ± 0.00805	0.03955 ± 0.00022	502505.92 ± 38294.94
R004	0.08959 ± 0.00009	10.39986 ± 0.00464	0.03936 ± 0.00018	689961.36 ± 14933.44
R006	0.08935 ± 0.00007	10.34925 ± 0.00542	0.03843 ± 0.00010	1367055.02 ± 34107.99
R008	0.0894 ± 0.00009	10.38017 ± 0.00617	0.03873 ± 0.00049	898314.62 ± 39148.11
Delta	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	
R002	0.23% ± 0.12%	0.26% ± 0.08%	3.33% ± 0.58%	
R004	0.14% ± 0.10%	0.23% ± 0.04%	2.84% ± 0.47%	
R006	-0.12% ± 0.08%	-0.25% ± 0.05%	0.41% ± 0.27%	
R008	-0.07% ± 0.10%	0.04% ± 0.06%	1.21% ± 1.28%	

Isotopic ratios and deviations from the certificate values of U isotopes measured as the dioxide species on an Si substrate.

This research will address two related issues that arise from our observations: the first is directly applicable to improving measurements for nuclear non-proliferation and forensics. We will determine 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. 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. Substrate materials were procured to mount uranium oxide particles with the appropriate doped trace elements. A cursory method was developed to produce SIMS substrates for silicon and gold materials. Purchased polished graphite substrates were also used. Finder-grids were evaporated on silicon and carbon substrates through an etched Mo mask to facilitate relocation of particles once dispersions were made, and initial results were obtained.

In FY 2012, research was conducted to verify that U isotopes measurements can be made as the oxide species on various substrates (Si and Au) without isobaric interferences. A table showing isotopic ratios and deviations from certificate values of U isotopes measured as the dioxide species on a Si substrate is shown. The data, taken on the PNNL Cameca ims-4f, show that deviations are close to zero, within the uncertainties. There is a small mass dependent bias, and the ^{236}U abundance is slightly high. This may be due to an improper interference correction due to the ^{17}O and ^{18}O. Variations are likely due to instrumental instabilities that have been remedied since data were acquired. In addition, sample mounts have been made to test the veracity of measuring the oxide species on gold versus the elemental ion species on carbon. Detailed results and their potential to customer requirements will be discussed elsewhere.

In the coming year, production prototype substrates will be produced and U isotope measurements with the dioxide will be repeated. Data from the University of California-Los Angeles will be analyzed and reports written on the results of the measurements. A small round-robin test may be initiated to test the method in FY 2013.

PN11041/2363

Light Source Photocathode Performance and Development

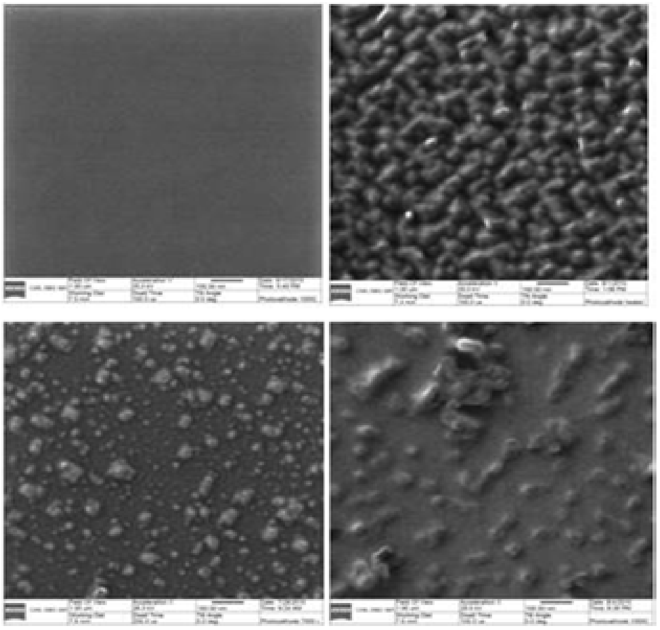
Wayne P. Hess

This project develops new research capabilities for testing existing photocathode materials and designs and 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 (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 goal is to increase photocathode longevity by understanding and modeling photocathode failure mechanisms. We conducted post-mortem analysis of used (expired) photocathodes from the Thomas Jefferson National Accelerator Facility Laboratory (JLab) and determined that the photocathode emission yield degrades under operating photo-injector conditions consistent with a model in which the surface Cs layer is removed from the surface by ion back bombardment sputtering.

In FY 2011, we completed post-mortem analysis of expired photocathodes that produced a manuscript published in *Physical Review Special Topics – Accelerators and Beams* in FY 2012. Highly detailed Rutherford back scattering spectrometry (RBS) results showed the photocathode lattice as highly crystalline despite surface roughening with no indication of bulk damage due to ion backscattering in the photoinjector chamber. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) results showed no ion implantation and light surface contamination, consistent with that introduced during sample handling under relatively clean conditions. The FY 2011 work prepared for further collaboration with staff at JLab. In particular, our helium ion microscopy (HIM) images (see figure) revealed that photocathode activation procedure leads to dramatic roughening of the photocathode surface, a surprising result that dramatically impacts electron emittance. The observed roughening, has lead us to propose a novel method for activation of GaAs photocathodes of the type used at the JLab. This activation makes use of arsenic capped GaAs wafers that we will test in FY 2013.


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.

Tools developed in FY 2011 contributed greatly to FY 2012 progress. We further tested the multi-source thin film deposition chamber by coating a clean Ag(100) single crystal with two monolayers of MgO and performing ultraviolet photoelectron spectroscopy (UPS) and angle-resolved photoemission spectroscopy (ARPES). The UPS results confirmed the work function reduction to near 3.0 eV measured previously on a polycrystalline test sample. We compared these results to UPA and ARPES from the clean single-crystal surface. We also produced a hybrid metal photocathode and plan to characterize mid-gap states.

In FY 2013, we will test the utility of thin films of various compositions to enhance quantum yield from Cu and Ag photocathodes and anneal samples to test F-center importance in the emission mechanism. We will activate a hybrid metal photocathode without high temperature treatment to avoid surface roughening and characterize photoelectron emittance and surface morphology using two microscopies. Finally, we will measure the effect on thermal emittance and, if warranted, transfer the technology to accelerator test facilities.

PN10050/2292

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

Hongfei Wang

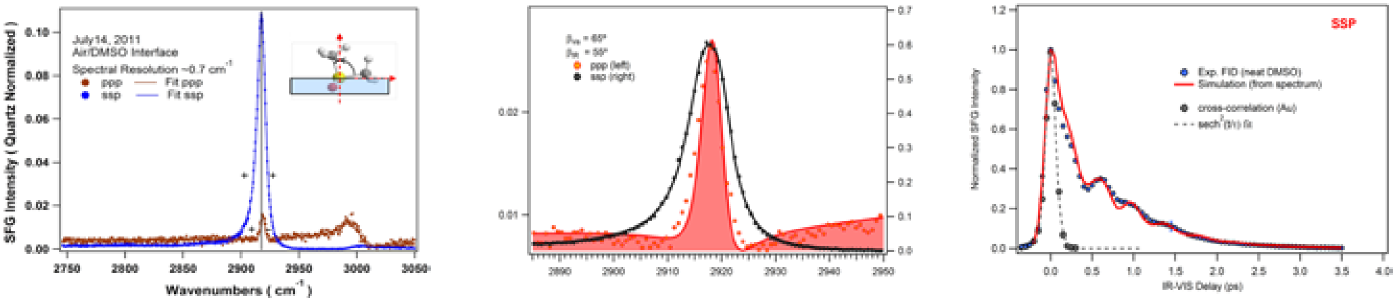
Using cutting-edge instrumentation, this project will lead to new discoveries in surface science and have broad applications on the characterization of structure and interactions at various molecular interfaces that are critical but elusive in many scientific and engineering fields.

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. This has been a growing field and is ready for exploring applications related to material and biological 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.

Specifically, 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 and a game changer that will 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.

We commenced work in 2010 to support experimental and theoretical studies applicable to various aqueous, non-aqueous liquid interfaces, and catalytic solid surfaces. The key to successful completion rests on the successful design, construction, and testing of the complete laser system; the

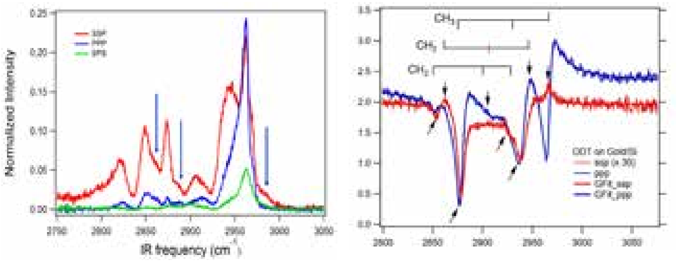


(a) (b) (c)

The HR-BR-SFG spectrometer enables measurement with unprecedentedly accurate line shapes in different polarization combinations, and the coherent vibrational dynamics can be accurately predicted using the spectral data. (a) and (b) For the air/dimethyl sulfoxide (DMSO) interface SFG spectra, 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 separation between peaks is 2.8 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 of the two methyl groups from the interface normal. (c) The coherent vibrational dynamics as probed with ultrafast SFG free-induction decay (SFG-FID) is quantitatively reproduced with the high-resolution spectral data. This demonstrated that the HR-SFG is not only a tool for spectroscopic and structural studies, but a powerful tool for dynamics studies. Such information has not been expected, and this development is expected to change the related fields significantly.

PN10058/2300

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. In FY 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. We successfully built the world's first high resolution broadband surface sum-frequency generation vibrational spectrometer (HR-BR-SFG-VS).



(a) (b)

HR-BB-SFG-VS as game-changing tool for complex surface spectral and structure analysis. (a) The HR-BR-SFG spectral of cholesterol at air/water interface. More than 10 overlapping peaks can be well resolved from the congested spectra. The polarization dependence can also allow unique assignment of the peaks. (b) Unique fitting in both ssp and ppp spectra of ODT self assembled monolayer on gold surfaces can identify 8 peaks, and their intensity and phase relationships allow determination of the conformation of the ODT molecule. SFG spectrum on metal surface is usually dominated by ppp polarization, and the ssp spectral line shape is usually unclear. With the high resolution SFG, the ssp spectral line shape is with excellent signal/noise ratio, allowing quantitative polarization and structural analysis for SFG on metal surfaces.

Spectral resolution is ~0.6cm^{-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 FY 2012, we have continued the research on various molecular interfaces focusing on the following aspects:

Pushing the limit for resolving spectral and structure details of relatively simple liquid and Langmuir monolayer surfaces. We showed that high-resolution SFG-VS can clearly capture spectral interference and phase relationship in closely overlapping vibrational peaks. Examples are demonstrated on the long-chain nonadecanenitrile ($C_{18}CN$) and the 4-pentyl-40-cyanoterphenyl (5CT) Langmuir monolayers.

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. For example, we resolved 8 peaks (versus 3 or 4 in the literature; see figure at left) in the C-H stretching vibration region for the octadecanethiol (ODT)/gold surface, and demonstrated how to perform polarization analysis on SFG spectra of molecules on metal surfaces. We also used cholesterol molecule as the example to show that high-resolution SFG can clearly identify spectral details in complex vibrational spectra. These point to the possibility to use the C-H vibrations as the new vibrational fingerprint region.

Exploring the dynamic information of surface molecules in the line shape of the high-resolution SFG-VS. We demonstrated that the peak intensity, position and width obtained from high-resolution SFG-VS line shape can quantitatively predict the coherent vibrational dynamics of surface molecules, including homogeneous and inhomogeneous broadening and interactions. Unlike the direct dynamics measurement that is limited to well-separated vibrational peaks, the frequency domain high-resolution SFG-VS measurement can be used for obtain such information for molecules with closely overlapped peaks. This shall greatly broaden the scope of dynamics analysis of molecular surface interactions.

These studies significantly moved the field of surface nonlinear spectroscopy forward, leading to a deeper fundamental understanding of the molecular interface. Most importantly, these results have shown that high-resolution SFG is a powerful tool that has opened new opportunities in surface/interface studies.

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

János Szanyi

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. With its high thermodynamic stability, CO_2 is the most underutilized carbon source in the production of high energy density organic molecules. To minimize the CO_2 chemical conversion energy requirement, heterogeneous catalysts with high production effeiciencies and selectivities are required. Thus, understanding the elementary steps of the reduction process and the nature of the active catalytic centers is necessary.

Transition metals alone have proven ineffective for the activation of CO_2, leading to the development of bi/multi-functional catalytic systems. In enzyme 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.

We are designing and constructing active sites for CO_2 reduction from two directions: well-defined metal clusters on oxides and multifunctional nano-scale clusters. These materials enable understanding of the metal oxidation state effects, 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. Multi-functional catalysts utilizing polyhedral siloxane building blocks will be designed synthesized and tested. These supramolecular architectures allow fine tuning and optimization of functionalities required for CO_2 reduction. The primary project goals for FY 2012 were the synthesis, characterization, and catalytic testing of selected materials, and the expansion of detailed kinetic studies to a number of catalysts.

The results of initial testing of Pd-based catalysts clearly showed that the selectivity toward the formation of CO and CH_4 can be varied systematically by changing the metal dispersion on alumina support. Palladium atomically dispersed on the oxide support catalyzed CO_2 reduction to CO with above 90% selectivity, while CH_4 was produced on large metal clusters with more than 90% selectivity. Catalytic testing of carbon nanotube-supported palladium catalysts revealed the critical role oxides play in CO_2 reduction. Our work this year focused on alumina-supported Ru catalysts, known to be active methanation catalysts. Based on Pd/Al_2O_3 system results, we examined the effect the Ru active phase dispersion on the activity and selectivity of Ru/Al_2O_3 catalysts. Measurements revealed that indeed, product selectivity toward CO and CH_4 varied significantly with Ru particle size: small ("atomically" dispersed) Ru centers produced CO with high selectivity, while CH_4 was the primary product on nm-sized Ru clusters. Apparent activation energy determined from kinetic measurements at low conversion levels systematically showed a ~20kJ/mol difference for CO and CH_4 production, suggesting different reaction mechanisms for formation of these two products.

We continued the synthesis of single metal ion sites supported on and incorporated into polysiloxane frameworks. We synthesized metallo POSS frameworks containing Ru, Pd and Ni species and developed synthetic methods and schemes to synthesize metallo POSS frameworks with bridging metals. Structural characterization of these compounds using solution NMR (^{29}Si, ^{13}C and ^{1}H) confirmed the existence of monomeric and dimeric compounds formed during the synthesis. We also continued evaluation of phosphine based RuPOSS complexes and studied the conversion of CO_2 to formate and monitored the conversion and kinetics by *in-operando* NMR spectroscopy. The catalyst synthesized reduced CO_2 at moderate rates with nominal TOF of 1-3 h^{-1}. This provided an evidence for proof-of-concept to demonstrate the catalytic nature of these compounds. Catalytic evaluation of the RuPOSS framework on heterogeneous supports was achieved by a two-step process: the RuPOSS complex synthesized was deposited into a MCM-41 framework by incipient wetness techniques, and the solvent was removed. We studied the conversion of CO_2 to CH_4 and CO under reaction conditions and compared it to Ru on Al_2O_3 at two different loadings.

Detailed kinetic studies on both oxide-supported heterogeneous and POSS-based metal catalyst systems, together with further spectroscopy characterization *in* and *ex situ* will be the focus of our research efforts in FY 2013. These studies should yield insight the mechanisms of CO_2 reduction of these catalysts.

PN11055/2377

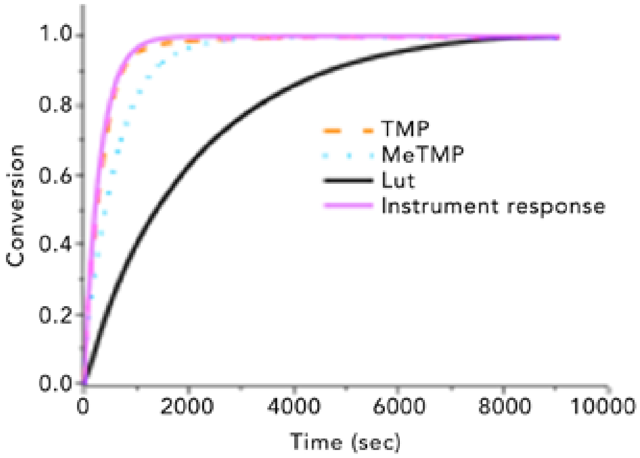
Non-Metal Activation of Hydrogen for Energy Storage in Chemical Bonds

Donald M. Camaioni

The activation of small molecules such as hydrogen, carbon dioxide, methane, and nitrogen is critical for the 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 the activation of hydrogen using transition metal catalysts is widely practiced, activation with non-metals is less common and little understood. This lack of understanding in turn hinders the development of new and inexpensive catalysts for potential energy storage applications. To resolve this problem, we have been 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 collective information will be used to develop simple, predictive relationships. In addition, we have been exploring the potential uses of this chemistry as a means of storing energy in fuels and chemicals.

For 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. 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. 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 BCl4-. Simultaneously, we had 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.



Time-dependent conversion data for reaction of $B(C_6F_5)_3$ with Lewis bases—tetramethylpiperdine (TMP), N-methyl-TMP (MeTMP) and lutidine (Lut)—in the presence of H_2, corrected for the calorimeter instrument time constant.

For FY 2012, we developed a new capability to extract the reaction rate constants for hydrogen activation by FLPs from the time dependence of the heat flow measured by isothermal reaction calorimetry. Our results were obtained by reacting nitrogen bases with *tris*(pentafluorophenyl)borane, $B(C_6F_5)_3$ in aprotic non-polar solvents (e.g., toluene and bromobenzene) under 100-psi H_2 gas. Our analysis of the heat flow traces showed that the rate information for the hydrogen activation step could in some cases be deconvoluted from the instrument response. A mechanistic kinetic model was developed to fit the heat flow data by least squares regression. Application of the model to the data for the reaction of H2 with lutidine/B(C6F5)3 in toluene at variable temperatures provided both rate constants and activation parameters for the activation step:

$$C_7H_9N + H_2 + B(C_6F_5)_3 \rightarrow [C_7H_9NH^+][HB(C_6F_5)_3^-]$$

This approach provided the first detailed experimental insight into H_2 activation by FLPs.

We also performed a computational study of H_2 activation and heterolytic dissociation promoted by prototype Lewis acid/base pairs NH_3/BX_3 (X = H, F, and Cl) to understand the reaction mechanism. Although the NH_3/BX_3 pairs form strong dative bonds, electronic structure theories make it possible to explore the potential energy surface away from the dative complex, in regions relevant to H_2 activation in FLPs. We find that structural reorganization of the precursor complex plays a significant role in the activation and that charge-transfer interactions are the dominant stabilizing force in the activated complex. Our detailed analysis of the interaction of H_2 with the FLP provides insight into the important components that should be taken into account when designing related systems to activate H_2. Our progress and results from our project work this year produced papers that appeared in both the *Journal of Physical Chemistry A* and *Dalton Transactions* publications.

OnSpec Advanced Condition Monitoring and Fundamental Research of Aggregation Precursors in Nuclear Materials Reprocessing

Tatiana G. Levitskaia

This project evaluates the potential of spectroscopic monitoring to detect organic phase aggregation in separation systems and define the analytical capabilities of an aggregation monitoring system (referred to as OnSpec).

This research contributes to the fundamental understanding of the formation of pernicious aggregation precursors that lead to third-phase formation, extractant oligomerization, and interfacial crud formation in liquid-liquid extraction processes, along with monitoring these precursors online (OnSpec). In liquid-liquid extraction separations processes, third-phase or interfacial crud pose significant operational and safety challenges and are associated with nuclear criticality concerns due to the potential accumulation of fissile material in equipment not designed to be critically safe. While previous research has thoroughly defined PUREX system parameters that encourage detrimental third-phase formation, a significant knowledge gap exists regarding similar processes in other separation systems and the progressive assembly of the aggregated species as precursors to the third-phase formation in general. To date, no efforts have been made to develop online spectroscopic monitoring technology for the prediction of the organic third phase.

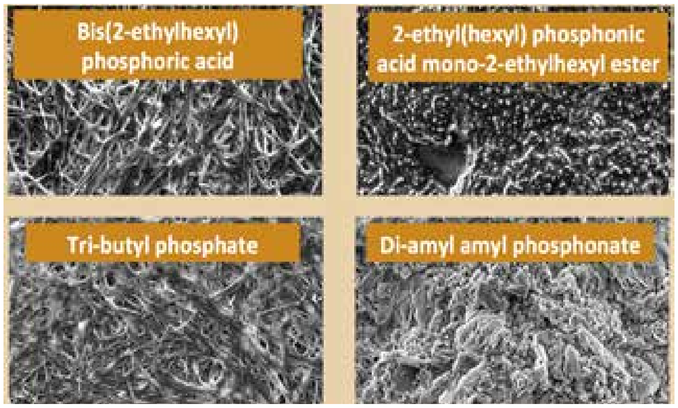
If developed, an OnSpec aggregation monitoring system will significantly enhance our understanding of mechanisms of the third-phase formation and pathways to maintain homogeneity of the extraction organic phase, eliminating associated criticality concerns and expanding the working operation range of the extraction processes relevant to the used nuclear fuel reprocessing. To achieve these goals, we have conducted studies under various conditions to examine the spectroscopic signatures of the aggregation precursors for both neutral and proton-ionizable organic ligands, which facilitate the transport of metal ion across liquid-liquid interfaces via ion-pair and ion exchange extraction mechanisms, respectively.

For neutral tri-butyl phosphate (TBP) extractant in *n*-dodecane solvent, the third phase formation upon contact with aqueous nitric acid (HNO_3) or plutonium-IV Pu(IV)/HNO_3 solutions was investigated by vibrational Raman/Fourier transform infrared (FTIR) spectroscopy or visible absorbance spectroscopy, respectively. For the first time, the spectroscopic signature of Pu(IV) in the heavy third phase was documented and reliably measured. This discovery can be used to develop online monitoring of plutonium speciation in reprocessing streams to prevent critical conditions. It was also observed that the increase in water concentration as measured by Raman spectroscopy with the associated increase in the conductivity of the organic phase can serve as indicators of the third-phase onset.

In another series of experiments, the mechanism of third phase formation using proton-ionizable bis(2-ethylhexyl) phosphoric acid (HDEHP) extractant in an alkane solvent was investigated. FTIR measurements indicated that high loading with trivalent f-metal ions (M^{3+}) results in the appearance of the bridged M^{3+}-HDEHP aggregates of progressively increased size, which serve as precursors to the third-phase formation. The observation that these precursors can be readily detected by FTIR spectroscopy opens a new opportunity of their online real-time monitoring. Raman measurements indicated changes in water bands in the organic phase upon formation of M^{3+}-HDEHP aggregates that can also be utilized for the monitoring purposed.

The effect of the phosphate versus phosphonate extractant functional complexing group on the formation of interfacial crud upon binding and high loading with M^{3+} was compared. The structural aspects of the formed cruds have been examined by scanning electron microscopy (SEM). In this study, the neutral and proton-ionizable phosphate and phosphonate ligands were evaluated. It was found that regardless of the M^{3+} extraction mechanism, phosphate extractants form highly ordered gel cruds, which adopt rod-like organization and readily retain water. In contrast, phosphonic ligands formed less organized gels with partially opened water channels. This result speculatively suggests that formation of the crud in the extraction systems can be manipulated by varying basicity of the functional group.

This project ultimately resulted in identifying the spectroscopic signatures of the third-phase precursors that can be utilized for the development of OnSpec aggregation monitoring system to enhance safety and operation control of the used fuel reprocessing flowsheets.



SEM images demonstrate that phosphate and phosphonate etractants form gels of different organization structure suggesting new pathways to maintain homogeneous organic extraction phase even at high loading conditions.

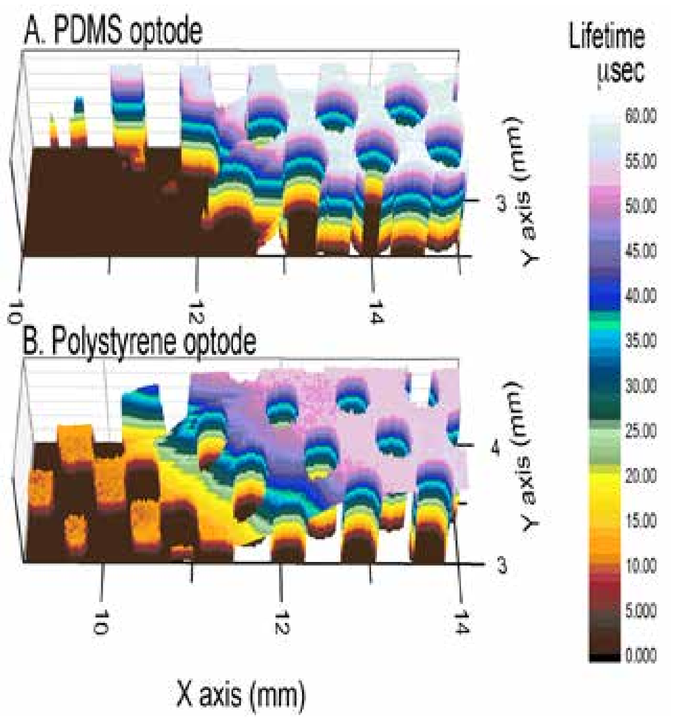
PN12060/2461

Oxygen Optode for Chemical Imaging in Microfluidic Microbial Models

Jay W. Grate

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 with chemically sensitive fluorescent dyes. With advances in optical imaging techniques and digital instrumentation, current optodes extend 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. Key parameters for chemical mapping include O_2, CO_2, and H ion concentrations, each of which can be sensed optically using fluorescence measurements, where optode material luminescence is dependent on the parameter of interest. These fluorescent sensors are designed to be reversible and thus respond to changes in the sensed parameter.



Fluorescence lifetime as a function of position showing pore network devices with optodes in either PDMS(A) or polystyrene(B) polymer. The selected region intersects a fluidically generated oxygen gradient.

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.

Early in the project, we considered a number of fluorophores known to respond to oxygen concentrations, and developed in in-house measurement capability for the fluorescence lifetime imaging of oxygen-sensitive fluorophores. As the project progressed, 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 in which the fluorophore is dispersed, and its oxygen 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 glass cover underside in contact with fluids in the micromodel can sense oxygen concentration in individual pores as well as detect fluidically-generated gradients along a line across the pore network width.

Research in FY 2012 focused on imaging oxygen gradients in two dimensions over microfluidic pore networks and developing a new microfabrication method for pore networks. Previous micromodels consisting of a glass cover plate over a dry etched silicon device containing the pore network can be imaged only from the cover plate side. The optode film was incorporated into this design by spin coating the film on the glass cover plate prior to bonding to the silicon device. Consequently, a continuous fluorescent film was present between the cover plate and pore network; using fluorescent microscopy imaging, the structure of the pore network was not distinguishable from the continuous fluorescent film. We developed a silico n-on-glass microfabrication approach to replace the dry etched silicon pore network.

PN09057/2225

This new method provides the precision advantage of dry etched silicon while creating a structure that is transparent across all microfluidic channels and pores, and can be imaged from either side. A silicon layer is bonded to an underlying borosilicate glass substrate and thinned to the intended height of the microfluidic channels and pores to be created. The silicon is then patterned and through-etched by deep reactive ion etching (DRIE), with the underlying glass serving as an etch stop. This glass base is transparent, while the nonetched silicon is opaque. A glass cover plate with the optode film can be bonded in the customary way. This device can be imaged from the glass base side, so that the fluorescent oxygen-sensing film on the glass cover slip can only be observed through the microfluidic channels where the silicon has been removed by the etching process. Thus, the fluorescent signal encodes the oxygen concentration in the channel, and the presence of a fluorescence signal reveals the microfluidic structure simultaneously.

Optodes were incorporated in the silicon-on-glass micromodels using a Pt porphyrin fluorophore in a polydimethylsiloxane (PDMS) film serving as oxygen-sensing layer and bonding surface or with Pt porphyrin a polystyrene film coated with a PDMS overlayer for bonding. In each case, 2D fluorescence lifetime images were recorded while fluidically creating a dissolved oxygen gradient from zero oxygen to 100% oxygen saturation. Representative images using our in-house scanning techniques are shown in the figure. The presence of opaque pillars between the observation direction and continuous fluorophore film yields images that retain defined spatial structure in the sensor image. This work has recently been published in *Lab Chip*.

The scanning method for fluorescent lifetime imaging is relatively slow because it measures fluorescence lifetime one pixel at a time. PNNL has purchased a Lambert LIFA-P fluorescence lifetime imaging system that uses a modulated LED and a CCD camera with a modulated intensifier that determines lifetime at every pixel in the image field simultaneously. With this capital investment, it will be possible to image the entire micromodel rapidly using the automated stage or follow dynamic processes at a selected image field. This system can measure the fluorescence lifetimes of long-lived oxygen sensing fluorophores, where conventional fluorescent lifetime imaging systems on microscopes measure only the lifetimes of short-lived fluorophores.

Probing Composition and Structure of Polarizable Reaction Mixtures Inside the Pores of Supported Metal-oxo Catalysts

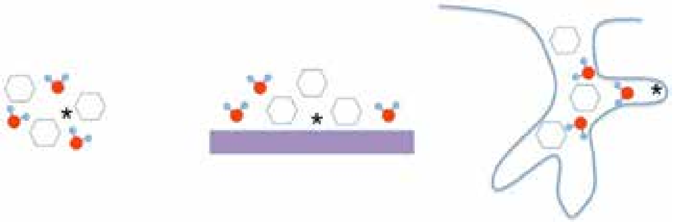
Robert S. Weber

We are combining PNNL advanced measurement, computational, and chemical synthesis capabilities to describe and understand those catalysts and their interaction with the reactants and products of biomass conversion.

The process of converting biomass into liquid fuel requires the use of catalysts to accelerate and direct the chemical reactions that lead from the original plant material to gasoline or diesel precursors. This project provides a way to quantify the detailed (molecular scale) composition and structure of liquid reactants and products in contact with a catalyst. The research will therefore help us understand one aspect of how the catalysts work and identify ways in which they can be improved. While there has been considerable research into the molecular structure of the catalysts themselves, much less is known about their interaction with their immediate environment. Because rates of chemical reactions depend on the concentrations of reactants and products, it is essential to measure those concentrations as locally as possible, preferably right at the catalyst so we can learn how to guide molecules to and from the catalytic sites. This project will yield those compositions and information about the orientation of molecules that can affect, or be involved in, the catalyzed conversion of the biomass into fuels.

We adapted a spectroscopy (measurement of light absorbed and emitted from catalysts) to study that immediate catalyst site environment (atoms that bind to reactants and products, lowering energy barriers that would otherwise slow desired chemical reaction rate). Light emission is familiar to anyone who has pasted glow-in-the-dark “stars” to the ceiling of a child’s bedroom. We are using color and decay rate of a related emitted light to study the motion and kinds of molecules that approach a catalyst site that absorb or emit light. We measure changes in spectra, particularly shifts in energies of spectral features (color) and changes in relaxation times on a scale comparable to molecule movements (millionths to billionths of seconds; glow-in-the-dark stickers relax more slowly, typically over many minutes).

In the 4 months since this project started, we completed three intertwined preliminary tasks in spectroscopy, materials synthesis, and modeling required to test and verify the underlying concepts upon which the project relies. First, we demonstrated that shifts in spectral features critical to project success are readily measured with equipment in hand. Next, we prepared the first in a series of four sample families whose detailed molecular structure is both known and can be modified in ways that will permit us to create models of materials that are functionally equivalent to actual catalysts. Finally, we performed calculations that relate state-of-the-art spectral features to the molecular structure and composition of the catalyst and its environment.



This representation shows a catalyst site (*) interacting with two different fluid molecules in three different types of confinement: in free solution (left), when the site is attached to a planar support (middle), and when the site is attached to the wall of a solid pore (right). The next stage of research will test whether we can describe differences in the structure of the fluid near the catalyst site, information that will help quantify each type of interaction.

Results show that the spectra are indeed sensitive to fluid composition near the catalyst sites and that the spectral shifts can be correlated to fluid polarizabilty. The principal component of fuel, hydrocarbons have low polarizability; water and alcohols have high. Because biomass to fuel conversion produces both types of fluids, we are confident that we will be able to distinguish when the catalyst is predominately neighbored by nonpolar hydrocarbons and when it is surrounded by polar compounds. Results can be used to help design supports on which the catalytic sites are attached; our calculations suggested model compounds that should exhibit a range of sensitivities to fluid polarizability. We unexpectedly found a very low solubility of some of our model compounds in nonpolar solvents. Going forward, we can exploit the insolubility as a way to purify and separate the model compounds. All three of those stages profited from prior work at PNNL. We further note that the project has rapidly combined four different disciplines: spectroscopy, quantum calculations, materials synthesis, and catalysis.

In FY 2013, we will advance these preliminary results to a more complex, realistic set of catalyst samples to learn how reactants and products interact with catalysts in three different degrees of molecular scale confinement: when the catalyst is free to diffuse among reactant and product molecules; when mounted on a flat surface; and when fixed to the wall of a microscopic channel or pore.

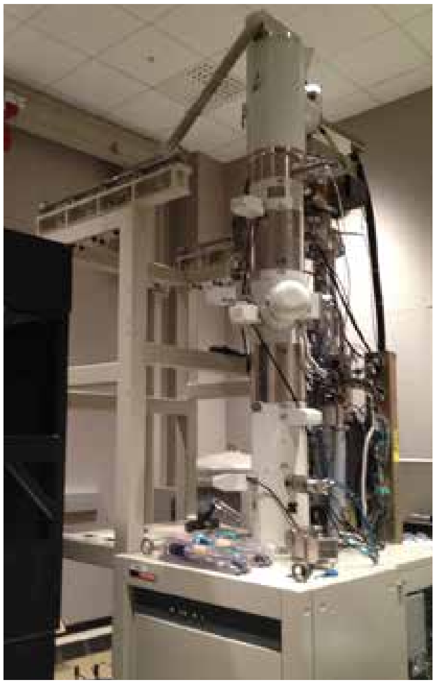
PN12062/2463

Probing Structural Dynamics with High Spatial and Temporal Resolution

Nigel Browning

We are developing a fundamental understanding of materials dynamics (from microseconds to nanoseconds) in systems where the required combination of spatial and temporal resolution can be reached only by the dynamic transmission electron microscope (DTEM).

This research will develop the DTEM capability to perform single-shot in situ measurements in liquid and gas stages with a combined spatio-temporal resolution at least four orders of magnitude faster than any other competing technique (including aberration corrected STEM/TEM). In this temporal regime, the DTEM is expected to have atomic spatial resolution, providing an in-situ TEM capable of studying nanoscale dynamic phenomena with several orders of magnitude time resolution advantage over any existing in situ TEM. In addition to providing unique insights into the inorganic and organic systems studied, this research will test the limits of temporal resolution and define electron optics and alignment for the next generation of truly ultrafast TEM (i.e., sub-ns). For nanoclusters in fluid around an electrode, interactions between the particles leading to the nucleation and growth of thin films will be examined for the first time. The ability to observe "live" biological systems will provide unique insights into biological systems.


The dynamic transmission electron microscope (DTEM)

The primary goal in FY 2012 was to move the DTEM from the University of California-Davis (UC-Davis) to PNNL and install the microscope within the EMSL Q-wing. This involved completing negotiations for the sale of the instrument to PNNL, organizing the move, and setting capabilities for the re-install. Thus far, the instrument has performed up to specification as a field emission microscope and is undergoing acceptance tests. The next stage of the installation is to build the two laser systems that will be used to drive the sample and create the pulsed electron beam (expected completion in November 2012).

In addition to the move and equipment installation, work commenced to develop new technologies for implementation within the instrument framework. The first of these technologies involved collaboration with the National Center for Microscopy and Imaging Research at the University of California, San Diego. The goal was to determine the ability of direct electron detectors to provide increase in the signal-to-noise over conventional CCDs and thereby increase the overall spatio-temporal resolution of the DTEM. Work here is expected to be completed by the end of September 2012 and show that a simple frame shifting device plus detector should be able to generate a frame interval of ~50 µs.

The second area of technology development involves building a complete model of the electron optical system to model the propagation of the large electron pulse within the electron microscope. Here again, the overall aim is to generate the understanding that will enable an increase in the spatio-temporal resolution. In the first year of this project, a collaboration was established with the University of Michigan and CEOS Ltd., the latter which is the manufacturer of the aberration correctors within the DTEM. The agreement to provide the key proprietary instrument parameters for the model has been accomplished and the expectation is that a complete model will be available by the time the microscope comes online in 2013.

The third area of research being addressed in this project involves the development of pulse compressors to be incorporated into a future microscope. Pulse compression is achieved through an RF cavity that effectively acts like a temporal lens. Collaborating with McGill University (which recently showed that a pulse of 10^7 electrons could be compressed to 80 femtoseconds), test parameters consistent with DTEM use were defined and will be used to determine the limits of spatio-temporal resolution.

For all of these projects, the first year of the program was design/initiation, where key experimental parameters for the DTEM were defined. After the successful move and microscope install, test parameters and understanding propagation of the electron pulse are underway and expected to coincide with the DTEM coming online in mid FY 2013. In addition, key staff members were employed on the project to develop the DTEM capabilities and operate the instrument.

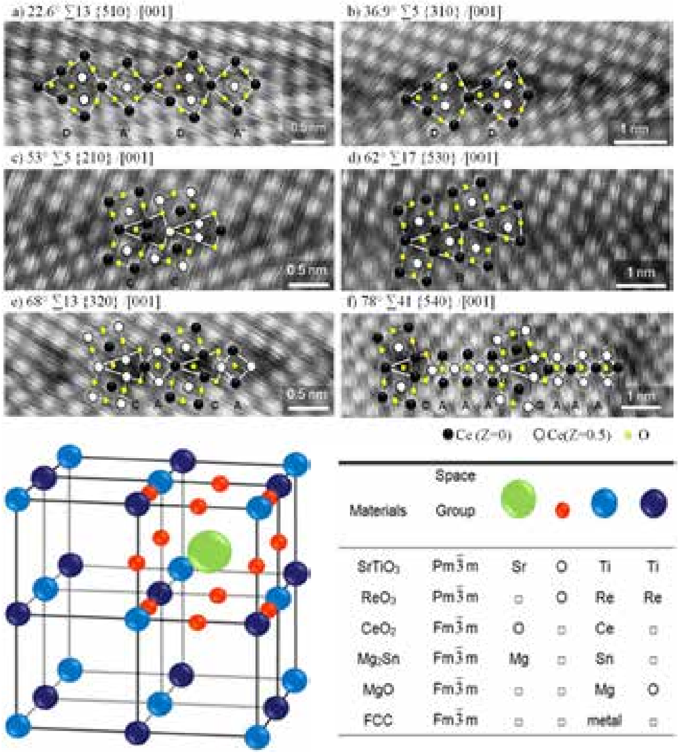
PN12063/2464

Quantitative Imaging of Atomic Scale Chemistry Changes at Interfaces

Nigel Browning

This research will develop the statistical methods necessary to quantify changes in the atomic structure and the chemistry that occurs at interfaces and in nanoparticles.

Interfaces control many of the structural, electronic, and chemical processes that take place in materials as well as the overall properties of a device or system. Using new imaging technologies, critical fluctuations in structure and composition controlling these properties can be observed and quantified, leading to a new level of understanding and control. Our approach will provide statistical validity to the presence of a particular structure, the number of impurities/vacancies present and the effect they have on the structure, thereby extending atomic scale analyses to the micro to macro scale important in real systems. Application of an *in situ* gas stage and environmental TEM will allow the stability of interfaces/nanoparticles to be quantified as a function of environmental conditions and identify likely pathways for structural instability. Such measurements applied together will significantly improve our understanding of the functionality of materials under real working conditions. The specific aim is to develop the framework for quantitative chemical imaging of interface/nanoparticle structures under environmental conditions (specifically under different ambient gas conditions). Quantitative chemical imaging has been applied only ad-hoc and has not been used for detailed comparisons between experimental results and first principles simulations. A quantitative framework for image interpretation is the only way to compare atomic-scale determination of interface structure and composition with larger scale property measurements.



Materials	Space Group	🟢	🔴	🔵	●
$SrTiO_3$	$Pm\bar{3}m$	Sr	O	Ti	Ti
ReO_3	$Pm\bar{3}m$	□	O	Re	Re
CeO_2	$Fm\bar{3}m$	O	□	Ce	□
Mg_2Sn	$Fm\bar{3}m$	Mg	□	Sn	□
MgO	$Fm\bar{3}m$	□	□	Mg	O
FCC	$Fm\bar{3}m$	□	□	metal	□

Images of [001] tilt grain boundaries show a set of structural units consistent with those seen in other fcc derived structures. The structural unit model for the grain boundary plane can be extended to multiple systems by simply observing the differences in atomic occupancies between structures.

In FY 2012, analysis focused on grain boundaries in oxides as a model system. Specifically, we studied a range of grain boundary structures in $SrTiO_3$ and CeO_2 and compared them to face-centered-cubic (FCC) metal structures to determine a set of rules for the formation of grain boundary structures. Such analysis has potential to create a set of crystallographic rules for interfaces that will allow the understanding of defect properties, and therefore the synthesis of new materials for specific applications, to proceed at a more rapid rate – the crystallographic rules will allow the defect properties to be predicted from the bulk structure.

Experimental results obtained from [001] tilt grain boundaries in CeO_2 show a systematic arrangement of structural units (dislocation cores) that show a remarkable similarity to those observed for $SrTiO_3$ grain boundaries and also the structural units seen in FCC metals (see figure). Similarities of these units in comparable coincident site lattice (CSL) grain boundaries can be related directly to an understanding of the densest packing structures of the parent crystal structures (i.e., because FCC metals $SrTiO_3$ and CeO_2 have the same symmetries in bulk compounds, their grain boundary dislocations will look similar). The atomic arrangement in FCC metals corresponds to the cubic densest packing of "hard spheres," identical modeling spheres packed so they touch, achieve the highest possible packing density in 3D space but do not penetrate. The CeO_2 structure can be derived from this form of densest packing by the filling of all eight tetrahedral voids with O ions and identifying the original four hard spheres of a unit cell of this packing with Ce ions. For the $SrTiO_3$ structure derivation from the cubic densest packing, these hard spheres must represent Ti and O ions and add an extra Sr ion in the center of the unit cell.

In crystallographic terms, presenting similarities between all three crystal structures by a single 2 × 2 × 2 superstructure (i.e., double unit cell of $SrTiO_3$ in all three dimensions) means that there must be *klassengleiche* subgroup-supergroup relationships (the full structure interaction is described by Bärninghausen trees). This can be represented pictorially (see figure), where crystal structures are plotted in only the upper-right front octant of the "superstructure cell." This octant also represents the whole unit cell of the entire $SrTiO_3$ structure. Unoccupied ion positions in CeO_2 and FCC metals are represented in the table by the "Schottky void symbol." Obviously, there are no unoccupied ion positions for $SrTiO_3$. For a representation of the CeO_2 structure, one needs to keep only those ion positions of the superstructure labeled as Ce in the accompanying table and put O ions into the centers of all octants. One then obtains the unit cell of CeO_2. The FCC structure is analogously obtained by the removal of all ions except those arranged in a face-centered cubic Bravais lattice.

Having derived the crystallographic origin of the similarities in structure, we can now use the understsnding to make structural predictions for other crystals. Also shown in the figure are the expectations for Mg_2Sn, MgO, and ReO_3. On the basis of their corresponding occupied ionic positions and Schottky voids in this table, one can predict structural units in high-angle grain boundaries. For identical grain boundary orientation parameters, the Mg_2Sn structural units will look "very similar" to the CeO_2 units. Besides possible differences in distortions caused by the presence of point defects in the boundary plane (something outside the crystallographic prediction but is the overall aim of this work), the main differences in units is due to ion replacement. Simply, this will be because the structures of the two compounds are those of anti-fluorite and fluorite structural prototype. Structural units of MgO will also possess similar "overall shape" as FCC structural units but will show additional O ions if the transmission electron microscope is sufficiently sensitive. Analogously, ReO_3 structural units will for identical grain boundary orientation parameters look similar to their $SrTiO_3$ counterparts with all Sr ions removed and possible differences in distortions.

The main result from FY 2012 has been identifying a classification scheme for grain boundaries in metals and ceramics based on the crystallography of parent compounds. This finding is important for future analysis of grain boundary properties as it allows the "base structure" of all boundaries to be predicted without the need for extensive experiments and simulations. In the materials used in energy technologies, these types of interfaces are key components in the overall properties. The properties themselves are typically characterized by ionic/atomic diffusion into and out of the interface structure. This characterization framework for interfaces means that future experiments that will be performed on individual grain boundaries can be related back to a more extensive set of systems based on the similarities between the structures and chemistries of parent compounds.

The goal for FY 2013 is to investigate the effect of cation doping on the grain boundary plane structure. Cation segregation at the interface is often used as a means to control the overall properties of the interface. We will investigate whether cations change the overall crystallography interface, whether it forms a completely different structure or is merely a chemical modification of the existing structure (similar to doping in the bulk system). Initial results from $SrTiO_3$ grain boundaries prepared to be intentionally doped with Pr and Eu suggest that dopants affect more than just chemistry. The presence of Pr in the structure seems to limit the grain boundary plane to one particular structural variant, a symmetric structure with no rigid body shift. This means that composition fluctuations in the nominally undoped grain boundary plane cause two equal energy structures to form while the intentional doping of Pr on the other hand can shift the energy balance to the symmetric boundary plane. The Eu doping has the opposite effect and pushes structural stability in the other direction. In addition, the structure is much more variable along the boundary plane.

Work is underway to evaluate the statistical prevalence of structures and correlate with energy changes at the boundary plane. These models for the single system will be extended to analyze effects on multiple similarly structured systems. Once these are complete, we will perform in-situ reduction/oxidation reactions to investigate the stability of this range of structures to the presence of oxygen vacancies. Such analyses will provide fundamental atomic scale insights into the mechanisms of vacancy/dopant incorporation in structural components involved in energy technologies such as battery electrodes and their effect on lifetime during cycling.

In addition to the scientific results, there were several efforts underway to improve the ability to obtain high resolution images by electron microscopy. This included the move of a JEOL 3000SFF from the University of California-Davis to PNNL. This microscope was successfully shipped and will be installed in FY 2013. Additionally, stages were purchased that will permit materials to be studied by tomography and while in-situ deformation takes place. All of these acquisitions will be employed during FY 2013.

The Statistical Mechanics of Complex Process in Bulk and Interfacial Environments

Marcel D. Baer

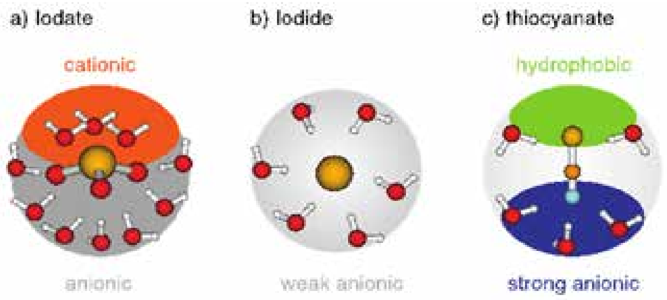
This project will develop new research capabilities for simulation of reactivity and structure in complex heterogeneous and homogeneous environments.

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.

In FY 2012, a joint experimental and theoretical study revealed the remarkable differences in the solvation structure around molecular HNO_3 under bulk and interfacial solvation, suggesting that hydrogen bonds between HNO_3 and water molecules at the solution surface stabilize the molecular form at low concentration. The same mechanism was postulated for the stabilization of molecular HNO_3 that occurs in bulk solution at high concentration. These results were published in the *Journal of Physical Chemistry B* and the *Journal of Physical Chemistry C* (with cover).

In a joint experimental and theoretical study, the first solvation shell structure about the polyoxyanion, iodate (IO_3^-), under bulk conditions as measured by extended x-ray absorption spectroscopy (EXAFS) was investigated. We found that one region of IO_3^- behaves like cation wherein the iodine atom has a formally positive charge while the other region behaves like an anion wherein the iodate oxygen atoms have formally negative charge. The physical picture that emerges from our study is that IO_3^- is indeed strongly and completely hydrated as a zwitterion. This revised understanding of the hydration structure of IO_3^- has implications in its ability to reside at hydrophobic interfaces, most notably the air-water interface and provides the first structural rational for counterintuitive behavior of why IO_3^-, ostensibly a large, weakly-hydrated anion, acts rather as a kosmotrope (structure-maker). These results were published in the *Journal of Physical Chemistry Letters*.



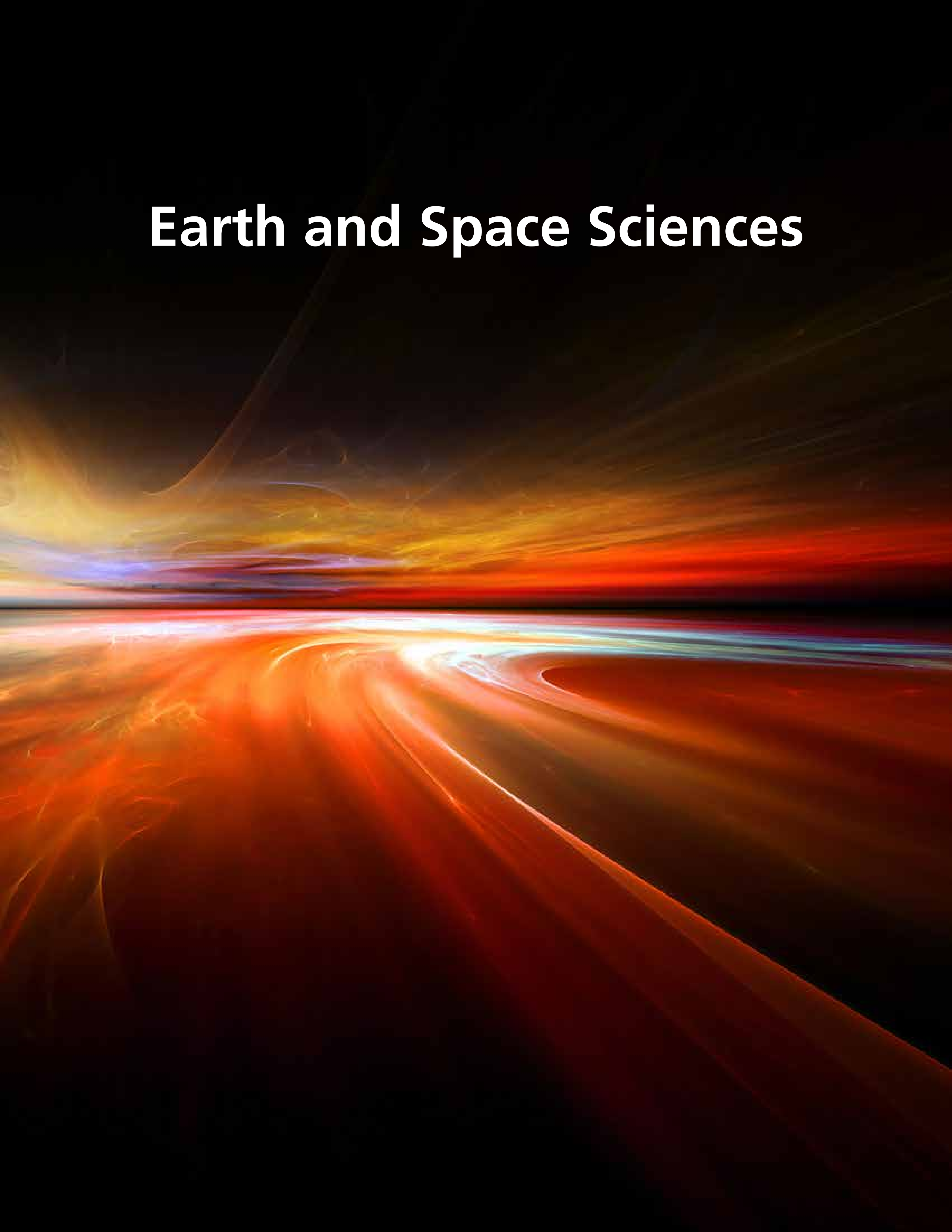
Schematic representations of the solvation of iodate, iodide, and thiocyanate.

We can further expand this concept and consider the role of the first solvation shell in determining/predicting interfacial propensity. To this end, we investigated three ions (iodide, iodate and thiocyante) with similar polarizabilities but significantly different surface propensities. We have studied their hydration structure under both bulk and interfacial conditions. Our results suggest that it is indeed the characterization of the hydration structure rather than the underlying polarizablility that is a strong indicator of surface propensity. These results are accepted for publication in the *Farday Discussions*.

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 (HCl, HBr, and HNO_3) and electrolyte solutions in bulk and interfacial environments.

PN11075/2397

Earth and Space Sciences



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

Mark D. White

This project is directed at 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.

Numerical simulation capabilities for modeling sequestration processes associated with the fate of greenhouse gases injected into geologic reservoirs has evolved rapidly during the past decade. Ten years ago, 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, non-isothermal 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.

Licensing requirements for CO_2 injection wells in the United States include numerical simulation to forecast the fate of the injected greenhouse gases and displaced host reservoir fluids. PNNL has developed a suite of subsurface flow and transport simulators, named STOMP, which include capabilities for modeling the coupled multifluid flow and transport, heat transfer, geochemical, and geomechanical process of geologic sequestration (THMC). The STOMP-CO_2 code provides the carbon-capture-utilization-sequestration (CCUS) community with an open-source simulator with capabilities for deep saline reservoirs with fully integrated THMC capabilities.

When properly applied, numerical simulators and their analytical tools provide a valuable understanding of complex geologic sequestration processes and have been invaluable in determining the suitability of sequestration projects. Historically, simulators are verified against analytical solutions, benchmarked against alternative implementations, or validated against laboratory or field experiments. Generally, all three checks are used during the simulator development process, with benchmarking and validation dominating, as the code becomes mature, through extensive application. Publications of code validations against laboratory or field experiments, simulator verification workshops and code comparison publications are all static snapshots of the state of numerical simulation science for greenhouse gas sequestration.

For the past two years, our project was involved with developing the dynamic framework and assimilating internationally recognized problems and numerical simulators for geologic sequestration into the framework. We completed a prototype framework that provided access to problems/case studies through a geographic or process map, the interface of which enabled users to locate specific problems/case studies via geologic location or source, with the process map locating these in a grid of coupled-process squares with increasing complexity.

The principal objective for progress in FY 2012 was to establish the PNNL-developed STOMP-CO_2 software as a world-class numerical simulator for CCUS applications. We approached this objective by 1) developing new innovative, integrated and open-source capabilities into STOMP-CO_2; 2) creating a suite of benchmark problems that were documented and incorporated into the Geologic Sequestration Software Suite (GS^3) collaborative computational framework; 3) growing the STOMP user community through short courses; and 4) acquiring funding for new code development cycles. From our efforts, four new capabilities were implemented into STOMP-CO_2. The underlying grid structure was altered to allow for faulted domains and internal boundaries. A trajectory-based fully coupled well model was developed that automatically transitions between flow and pressure controlled injections. An open-source rigid-body spring method based geomechanics solver was fully integrated into STOMP-CO_2 without requiring an independent grid. The vertical-equilibrium modeling approach was incorporated into the simulator in a manner that provided full or hybrid implementations for code users. The mathematical formulation, application use, and benchmarking of STOMP-CO_2 were documented in a PNNL report and released to the public. Project staff from PNNL held three STOMP-CO_2 short courses during this fiscal year: in UAE, Korea, and at the U.S. Environmental Protection Agency in Chicago, IL.

In summary, this research developed new critical simulator capabilities, created a collection of benchmark problems for geologic sequestration in deep saline reservoirs, educated users in the software application, and documented the software and benchmark problems, the latter of which have been incorporated into a new computational framework for collaborative projects in geologic sequestration.

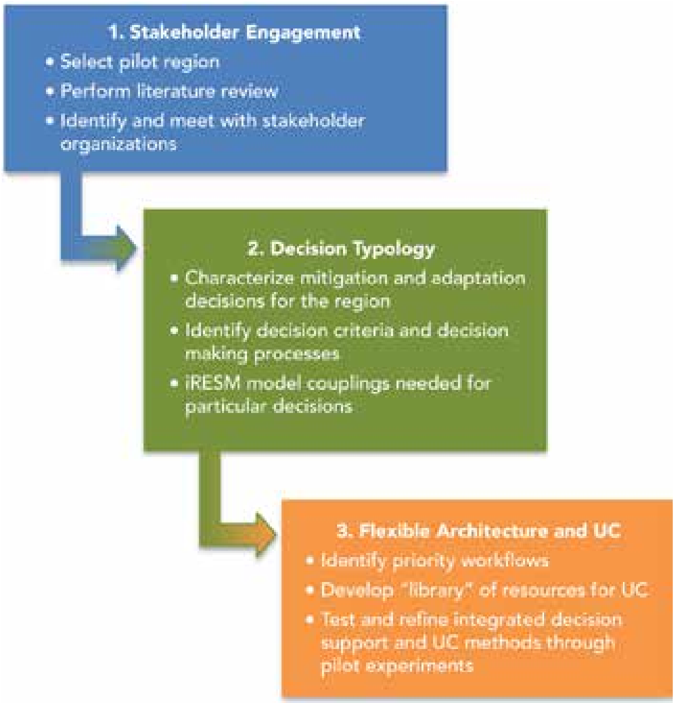
PN10014/2256

Decision Support Research for Integrated Regional Earth System Modeling

Richard H. Moss

> ***This project is researching what uncertainties matter most in different decisions, what information users want regional models to provide, and how information can be presented in the context of uncertainty.***

Regional decision makers trying to make sound climate change mitigation and adaptation decisions face a wide and complex array of uncertainties that span human and environmental earth systems. Because most of these uncertainties will not be reduced or resolved until after key decisions are made, regional planners face the conundrum of how to proceed with imperfect information. Decision makers need analytical tools and information to help navigate decision complexity and information uncertainty. This project is developing a prototype strategy for relating model results and information about uncertainty from integrated regional earth system models (iRESM) to different decision-making processes, including risk communication methods (graphical, visualizations, mock deliberative processes, etc.) that convey uncertainties relevant to specific questions or decisions. Previous case study research with stakeholders has identified specific information needs, but further work is required to categorize these needs more generally, relate them to decision making frameworks, and identify standardized model couplings and work flows to meet information requirements.



Relating the knowledge base regarding adaptation and mitigation decisions to model development. Results will identify frequently used decision criteria and guide experiments and identification of standardized workflows.

Specifically, our project is continuing research on stakeholder information needs in the Midwest pilot region, using these data to create a typology of decision criteria and decision making processes. We are reviewing the project's decision support methods, including the use of model-based scenarios of future conditions. The results will be used to plan a pilot decision support process for iRESM and contribute to the literature on scenarios in adaptation and mitigation decision making. In addition, the project has developed a knowledge base of the breadth and depth of Midwest mitigation and adaptation decisions, with the results published in the journal *Mitigation and Adaptation Strategies for Global Change*.

Key concerns for the Midwest region decision making include renewable portfolio standards, biofuels production, hydrology in the Great Lakes Basin, water availability, extreme precipitation/temperature events, and changes in long-term averages. Adaptation alternatives are being evaluated for water resources, urban infrastructure, transportation, agriculture, recreation, ecosystems management, and forestry. Mitigation decisions concentrate on the electricity sector, buildings, transportation, agriculture, and forestry. Based on a review of both peer-reviewed and grey literature, as well as interviews conducted with over 100 individuals spanning these interests, the team focused on energy and water, and developed and coded relevant variables: types of decisions, use of a formal framework such as cost-benefit analysis, criteria for decision making, and decision making processes. In addition, the team investigated decision support systems, including decision theaters and their effectiveness in presenting model results in decision making processes.

During FY 2013, the decision typology will be extended to other regions and issues and then linked to standardized iRESM model configurations to address the most common decision variables and interests identified in the literature and interviews. A white paper on decision support options for regional adaptation and mitigation decision making will be prepared. In addition, results will be used to plan initial numerical experiments with the iRESM framework as well as a decision support experiment using iRESM outputs.

PN12019/2420

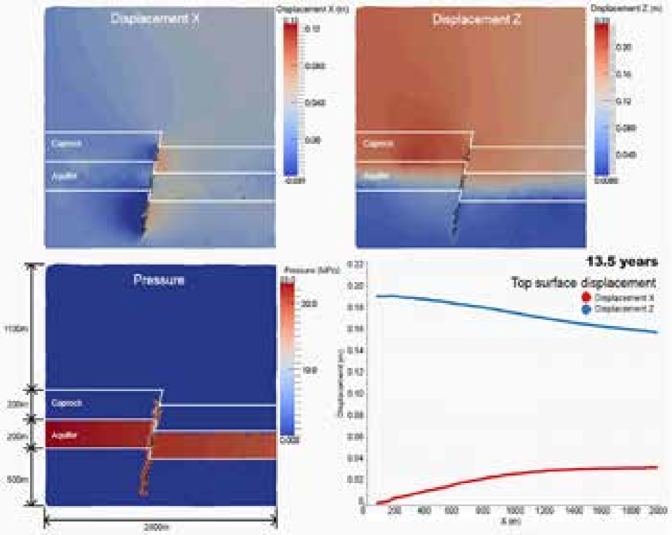
Development of Coupled Flow, Thermal and Geomechanical Capability for Carbon Sequestration

Yilin Fang

This research is developing critically needed geomechanical capabilities to address key research issues in 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 potential CO_2 leakage through the cap rock and overburden, which can lead to CO_2 release into shallow potable aquifers or 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 CO_2's long-term subsurface containment.

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 $scCO_2$ beneath the caprock on structural integrity.



Contours of horizontal displacement, vertical displacement, fracture locations, and fluid pressure in the DEM simulation domain, as well as displacements at the ground surface after 13.5 years of injection.

Our first steps incorporated a geomechanical model from the linear elastic theory into the existing parallel subsurface non-isothermal, 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.

In FY 2012, we made some improvement on the geomechanics code, Rigid-body Interface Element Method (RIEM), which has been incorporated into the existing parallel subsurface nonisothermal, multiphase flow and reactive transport code (eSTOMP-CO_2) for linear and nonlinear problems. The model was applied to an Aquifer Storage and Recovery site to simulate ground deformations. We initiated model development of Discrete Element Method to simulate coupled flow and geomechanics. A fracture propagation problem within a faulted domain during CO_2 injection was tested using this model. Coupled DEM and continuum scale model was explored using Open Source Finite Element Software Elmer to facilitate eventual coupling with geomechanics code in eSTOMP-CO_2. We also explored caprock permeability and thermal effect on caprock stability using Elmer. Two manuscripts on this research have been submitted. To date, our research has produced a paper in *Computers and Geosciences* on the analytical model to solve geomechanical modeling of CO_2 geological sequestration, which considers the poroelastic effects and accounts for the two-way coupling between the geomechanical response and fluid flow. We also submitted a manuscript describing the implementation of RIEM, and we contributed another on the application to the ASR site.

In FY 2013, we will continue testing the DEM model and developing method to couple DEM with RIEM. We will implement fracture and plastic model in RIEM. The models will be applied to potential field sites: storage site for FutureGen 2.0 and Wallula basalt pilot site.

PN11025/2347

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. This component includes coupling state-of-the-science community models of the regional atmosphere, ocean, land, and sea ice through a flux coupler to represent regional earth system processes and their interactions. Representations of land use and water use are to be added to interact with the natural water cycle to characterize regional human-earth system interactions that are critical for projecting regional climate change.

The second component includes developing a fully integrated environmental system model for iRESM 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, a model is being developed to represent hydrology, soil, managed and unmanaged ecosystems, and biogeochemical processes in a single modeling framework. Based on the Community Land Model (CLM), this 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. For scalability, a distributed extension of CLM (DCLM) has been developed to 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. Below, we summarize the progress made in each area of model development.

Regional Earth System Model (RESM). In FY 2012, we continued our work from last year, progressing in several areas. On developing a prototype RESM, the Weather Research and Forecasting (WRF) model was coupled with CLM through a flux coupler. After testing the model over the western United States in FY 2011, we shifted the testing over a North American domain at 20 km grid resolution. A simulation is being performed with boundary conditions from the NCEP/DOE global reanalysis for 1979–2005. The same model configuration was used to perform simulations driven by large scale conditions from the NCAR Community Climate System Model (CCSM4) for current (1975–2005) and future (2005–2100) climate. Preliminary analysis shows that the WRF-CLM simulation compares quite well with observations and is similar to the WRF-Noah simulation except for a somewhat larger warm bias.

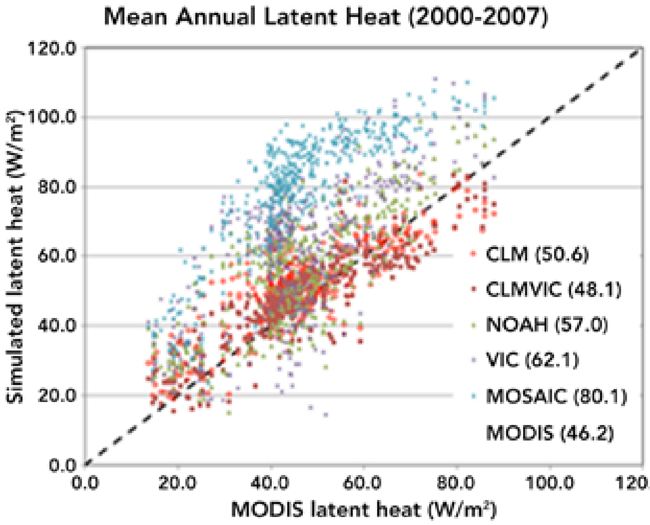
Land Surface Modeling. CLM has been selected to provide a consistent modeling framework with for modeling land surface and carbon cycle processes across the global model (CCSM), regional model (WRF), and spatially explicit models that will be coupled with energy infrastructure and operation models. To enhance the CLM capability 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-characteristic of the slow-varying base flow processes. These results were published 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-degree resolution. Simulations have been performed for 1979–2008 for comparison with observations and simulations by other land surface models that are part of NLDAS-2. Our results showed that CLM and CLM-VIC generally outperform

PN10027/2269

other NLDAS-2 models in simulating latent heat (LH) flux and runoff compared to the MODIS satellite retrieved LH and runoff from the MOPEX river basins. The figure below shows a comparison of simulated and observed LH at each MOPEX basin, showing the closest agreement between CLM-VIC with observations. A paper is in preparation to summarize the results for submission to the *Journal of Hydrometeorology*. 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 and the Midwest. Simulations have been performed for 1979–2008 for comparison with observations and the simulation over the regularly gridded NLDAS-2 domain for the same region.

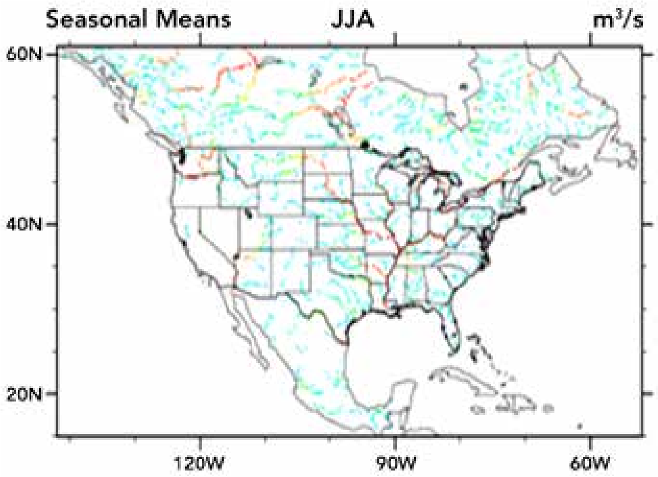
To understand the sensitivity of CLM to hydrologic parameters in the model, a study has been performed to apply an uncertainty quantification framework to identify key parameters that the simulated surface heat fluxes are most sensitive to. The results suggest that the three parameters associated with subsurface runoff in CLM lead to the largest uncertainty in simulating surface heat fluxes in a number of flux tower sites across the United States.



Comparison of observed latent heat from the MODIS satellite and the simulated latent heat flux from five land surface models including CLM and CLM-VIC and three other models (NOAH, VIC, and MOSAIC) that are part of the North American Land Data Assimilation System (NLDAS-2). Each point corresponds with observation/simulation at one MOPEX basin in the United States. The average latent heat fluxes for the models and MODIS are shown by the numbers at the bottom right.

River Routing Model. A new river routing model was developed and tested over the Columbia River Basin during FY 2011 with the goal of providing a more accurate river routing model to support grid- and subbasin-based CLM implementations and for coupling with a water management model. The new river routing model, Model for Scale Adaptive River Transport (MOSART), used a hierarchical river tracing method to construct river networks as well as 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 River Transport Model (RTM) developed for CLM have been used to simulate streamflow over the CRB at 1/2- and 1/16-degree resolution. The simulated streamflow produced by the new model compares much better with naturalized streamflow than RTM. A paper that describes the new model and its performance has been submitted to the *Journal of Hydrometeorology* and is undergoing revision. In addition to applying the new river routing model at regular grids, the model is testing using the subbasin approach. Preliminary results show that the model works well with both the grid- and subbasin-based approach, yielding similar results far superior than the RTM for larger river basins where river routing is important for correct simulation of monthly streamflow.

As noted, MOSART has been coupled to CLM so that it can be used in a fully integrated RESM framework and for modeling river routing in the offline CLM model with water management.



An example of seasonal mean streamflow simulated by the coupled CLM-MOSART over the NLDAS-2 domain.

Water Management Model. A water management model has been developed in FY 2012 to simulate the effects of reservoir operations on streamflow. The water management model includes two main modules: regulation and local extraction. The regulation module extract water at the reservoir based on water storage, regulation that follows monthly operating rules for flood control, environmental flow, irrigation and hydropower, and constrain extraction by daily partitioning of reservoir releases for irrigation water supply and other consumptive uses and environmental constraints. The local surface water extraction module extracts water at the model unit from hillslope surface runoff to represent irrigation retention ponds and from the main stem at the model unit if it is unpounded by an upstream reservoir. The model has been applied to the Columbia River Basin to simulate the regulated flow for comparison with observed streamflow. More refinements are being developed and implemented to improve the performance of the model. In addition, a paper will be prepared to describe the water management model.

The water management model has been fully coupled with MOSART to model the effects of water management on streamflow. An important water use in many regions is irrigation, so the new irrigation modeling capability in CLM has been tested by performing simulations over the NLDAS-2 domain. The simulated irrigation water amount is being compared with data to assess the realism of the irrigation model.

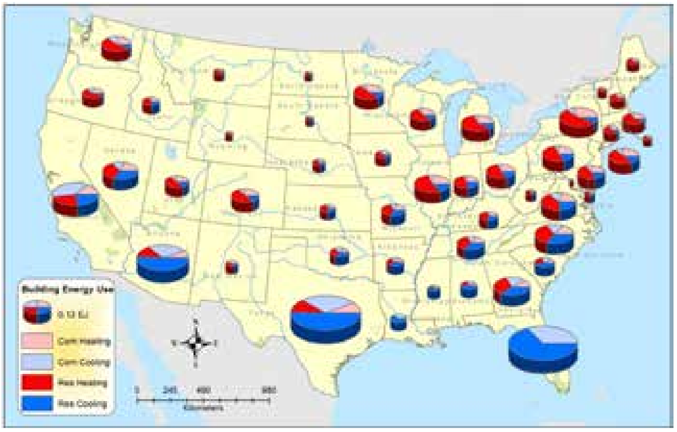
Development of Regional-Global Climate Assessment Model

Leon E. Clarke

This project creates a new, unique modeling capability to explore climate change and its responses, resulting in a regional integrated model to enable analysis at sub-regional scales (such as states or provinces) in an integrated framework explicitly linked to global-scale phenomena.

This research 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 relevant human and natural processes are brought into a single computational framework; i.e., 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 carbon cycle. Although integrated assessment modeling has a history at the global scale, there is no regional level integrated assessment model or modeling projects. This project will build such a regional scale integrated assessment model within the context of a global modeling framework. We are maximizing the fact that PNNL uses the 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.

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. 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. In addition, the RGCAM model will require linkage to a range of other modeling tools (e.g., detailed land use, regional climate, and electricity models), all of which operate at temporal scales well below 15 years. The code and a range of model input developments were completed, with the new capability included in the GCAM core version. In FY 2011, a fully subregional capability for modeling building energy was completed, along with an exploratory version of a 50-state version of the model. The code developed to create the buildings facilitated development of additional subregional sector representations.



Heating and cooling energy demands late in the century, under the assumption of no efforts to constrain carbon emissions.

In FY 2012, the prototype version of the RGCAM, 50-state buildings model created in FY 2011, was made a fully functioning model. This included bringing in a new representation of energy service demands that explicitly allowed for the consideration of changing heating and cooling degree days over time. The model was then utilized for other experiments, including uncertainty analysis and sensitivity analysis exploring the implications of different technology assumptions, long-term climate goals, and climate model outputs. Beyond the buildings model, there were further developments to elements of the 50-state regional capability in RGCAM, including industrial energy demands, transportation demands, and electricity generation. A r-based data system was developed to take data from a variety of data sources and seamlessly balance it to create 50-state assessments of these systems for use in GCAM. In addition to work on GCAM, the BEND model was completed, which provides explicit modeling of adaptation and mitigation in fine detail within buildings. BEND permits a user to develop a population of representative buildings for a geographic region, calibrate those buildings to actual historical weather and energy consumption, and accurately project energy consumption under a variety of different climate and technology scenarios. Finally, data protocols were developed for calibrating RGCAM and BEND for use in coupled experiments in other portions of this project.

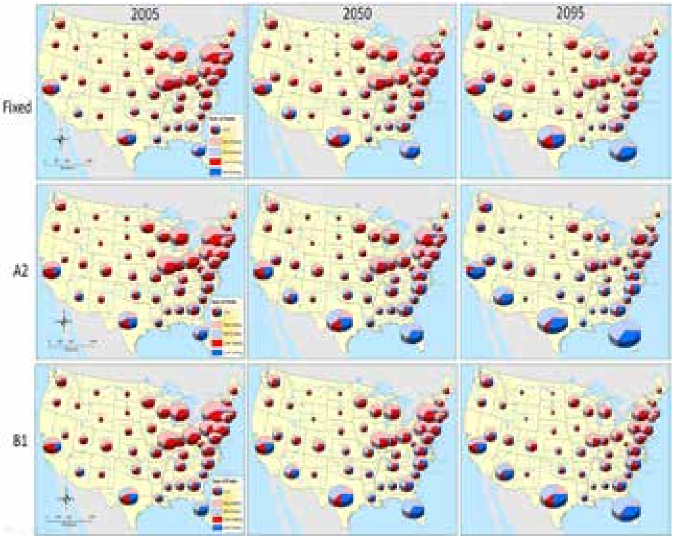
PN10030/2272

Exploration of Human and Environmental System Interactions due to Renewable Technology Penetration in the Midwest Pilot Region

Jennie S. Rice

We are demonstrating the capability of the integrated Regional Earth System Model (iRESM), bringing together results of individual modeling efforts with the results of the stakeholder decision support and uncertainty characterization research.

The iRESM is premised on the hypothesis that climate change, climate policy, and the mitigation and adaptation actions taken in response will produce critical interactions between human systems and land, water, and energy resources that can only be revealed through integrated, regional scale modeling. These interactions may be synergistic or antagonistic and, as such, may indicate the feasibility or infeasibility of certain mitigation or adaptation alternatives. We will demonstrate the iRESM framework capability through a series of numerical experiments simulating regional climate change, regional mitigation and adaptation decisions, and the associated impacts on the land-water-energy nexus, while also accounting for the modeling uncertainties inherent in the simulation. A one-of-a-kind multi-scale, multi-domain modeling system under development since 2010, the iRESM encompasses a multi-year effort designed to conduct a series of increasingly complex experiments to exercise various model couplings within the framework.



Heating and cooling energy use (2005, 2050, and 2095) in scenarios without climate influence ("fixed") and for the CCSM3 A2 and B1 scenarios in the CMIP3 archive. The A2 scenario reflects increasing annual carbon dioxide emissions worldwide, whereas the B1 scenario reflects an eventual decline in annual emissions after 2050.

During FY 2012, the project conducted a series of Phase 1 experiments to identify the climate signal in the midwest pilot region and explore the impact of that signal on building energy demand, its subsequent impact on the overall energy economy, and on crop productivity by coupling the regional climate model to various models within the framework. The project also initiated its first Phase 2 experiment to demonstrate the iRESM uncertainty characterization (UC) process. A primary accomplishment of the project this year was development of coupling strategies between regional climate modeling and the building energy demand model, the regional integrated assessment model, and the crop productivity model. These couplings were a necessary first step before the initial experiments could begin. To represent a range of climate futures in the uncertainty characterization process, we are using statistically downscaled climate data from Phase 3 of the Coupled Model Intercomparison Project (CMIP3) used in the fourth Intergovernmental Panel on Climate Change (IPCC) assessment report and dynamically downscaled simulation results for the new Representative Concentration Pathways (RCP) being used in the upcoming fifth assessment. The RCP simulations are produced with the regional earth system model developed as a key model component of the iRESM framework.

The model couplings between climate and other iRESM models are challenging because the different climate datasets provide different sets of variables and use different spatial and temporal scales, while each of the downstream models has particular climate data needs at particular scales that do not necessarily match what is available from the climate datasets. This project produced a set of integration codes and scripts that perform necessary variable, spatial transformations to accomplish the model couplings and tested the couplings in the Phase 1 experiments. The couplings are repeatable and flexible for use with additional climate simulations in similar formats, facilitating the exploration of uncertainty from model parameterization, model choice, downscaling method, and emissions scenario.

Of the various Phase 1 experiments conducted in FY 2012, the coupling of climate to state-level building energy demand in the regional integrated assessment model produced the most significant results. It demonstrated not only that climate has a significant impact on building energy demand at the national scale, but also that this impact exhibits large spatial heterogeneity across states. In the experiment, the climate change impact on heating and cooling demand in the 21st century is measured through estimating heating and cooling degree-days (HDD/CDDs) derived from gridded climate data for two future greenhouse gas emissions scenarios and comparing the results to HDD/CDD calculated without climate drivers and based only on the influence of socioeconomic development, technological change, and energy service expansion on historical levels. The figure indicates the spatial pattern of building energy use by state for these three cases. The scale impact in building energy use modeling emphasizes the importance of developing a building energy model that represents socioeconomic development, energy service expansion, and their interaction with climate change in a spatially explicit manner.

In the Phase 2, UC experiment begun during FY 2012 expanded on the Phase 1 experiment described above (involving climate-driven building energy demand in the regional assessment model) to demonstrate the application of the stakeholder-driven UC process to a policy decision regarding future building standards. For FY 2012, the focus was demonstrating how the identification of a particular stakeholder decision and associated decision criteria, along with the use of fractional factorial sensitivity analysis, provide an efficient way to identify key modeling uncertainties to pursue with uncertainty propagation. Without such an approach, analyses conducted in another project have shown that the dimensionality of the uncertainty characterization across the integrated framework becomes too unwieldy and results in prohibitively long run times, even in a high performance computing environment.

The decision context for the UC experiment involved three alternatives for future building energy codes and appliance and equipment standards: no change, standards resulting in a 50% reduction in energy use by 2050, and standards resulting in an 80% reduction by 2050. The initial decision criterion for comparing the alternatives was residential and commercial building services costs per square meter of floorspace. While broader sets of uncertainties (and decision criteria) will be addressed in later experiments, the demonstration nature of this experiment dictated that the project identify a relatively small set of relevant modeling uncertainties for testing with the fractional factorial sensitivity analysis approach. The uncertainties selected were population growth, rate of growth of economic output (GDP) per worker, future carbon dioxide emissions, and choice of general circulation (i.e., global climate) model (GCM). The analysis utilized three scenarios (low, medium, and high) for population growth and for GDP per worker, two future emissions scenarios (A2 and B1), and three GCMs. A full factorial analysis would require 162 cases, whereas the fractional factorial approach focuses on the five first-order cases (includes the policy variable) and the ten second order pairwise interactions.

The experiment compared the performance of the fractional factorial analysis to the full factorial with analyses of variance and determined that the fractional factorial explained over 99.9% of mean squared error, demonstrating the efficiency of the fractional factorial approach for this example. In addition, the results indicated that just two of the four modeling uncertainties (future carbon emissions and rate of GDP growth) explain over 98% of the variance. This result shows that only these two uncertainties should be carried through into the uncertainty propagation phase. Moreover, the overall reduction in the dimensionality of the UC was significant for this experiment: an order of magnitude reduction in the number of sensitivity cases to be run (162 vs. 15) and the number of variables for which probability distributions would need to be developed was reduced by half.

In FY 2013, the continuing UC experiment will develop and apply uncertainty propagation methods for the iRESM framework. Additional Phase 1 experiments are planned comparing the impacts of the RCP and CMIP3 simulation results. Also, the project plans a series of Phase 2 model coupling experiments. These will couple the regional integrated assessment model with each of three sector models (building energy demand, crop productivity, and energy infrastructure), all also coupled with climate. These experiments will address particular stakeholder interests from the Midwest pilot region, investigate alternative coupling strategies under uncertainty, and demonstrate the multi-scale, multi-domain modeling capabilities of the iRESM framework.

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

Lai-Yung (Ruby) Leung

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).

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. 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 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.

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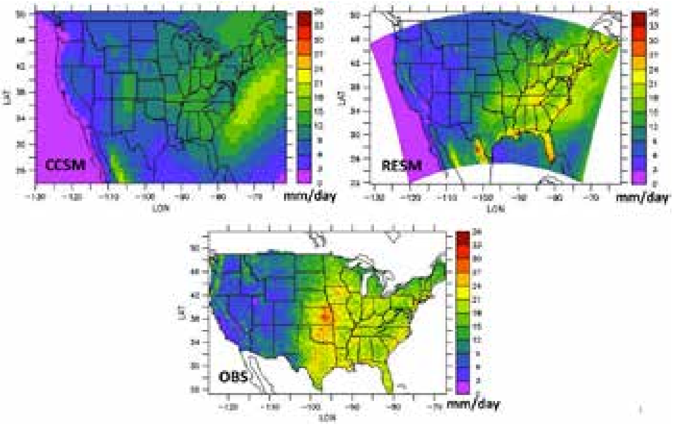
In FY 2010, the team adopted the region definition used in the U.S. National Assessment, dividing the conterminous states into Northwest, Southwest, Great Plains, Midwest, Northeast, and Southeast. The Midwest emerged as the region of choice for the first pilot study because it represents significant 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.

In FY 2012, progress has been made by different modeling teams toward the first phase model evaluation. This report summarizes examples of model evaluation efforts and highlights some key results.

For RESM, a simulation has been performed with WRF-CLM (i.e., RESM with prescribed sea surface temperature rather than interactive ocean) driven by large-scale conditions from the Community Climate System Model (CCSM4) for the current climate (1975–2005). The figure shows a comparison of observed and CCSM and WRF-CLM simulated 95th percentile precipitation during summer, showing with

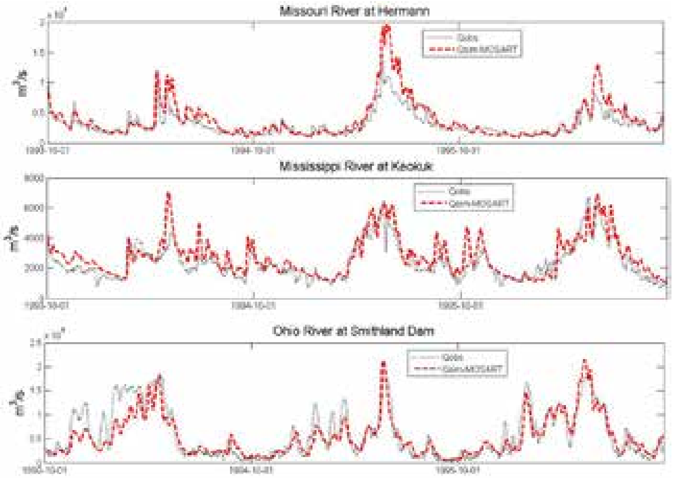


Observed (bottom) and simulated 95th percentile precipitation from CCSM4 (upper left) and WRF-CLM (upper right) in mm/day for the June-July-August averaged over 1975–2004.

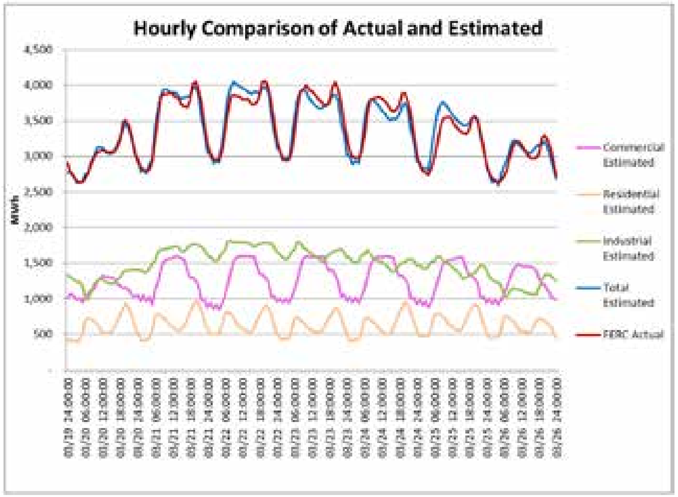
increased grid resolution, WRF-CLM simulated larger intense precipitation than CCSM and compared better with observations.

The Community Land Model (CLM) has been applied to the Midwest pilot study region at 1/8-degree resolution using both grid based and subbasin based configuration using NLDAS-2 atmospheric forcing. Extensive analyses are being performed to evaluate the simulations using observations and compare the grid based and subbasin based approach to understand their pros and cons at different resolutions and river basins with different climate/hydrology regimes.

The new river routing model, Model for Scale Adaptive River Transport (MOSART), has been applied to the Midwest pilot study region. The figure shows a comparison of the simulated streamflow at different stream gauge stations when MOSART was driven by runoff generated by NLDAS-2 models. The results show reasonable agreement with observed streamflow in basins that are not strongly influenced by human activities.



Observed (black) and simulated (red) monthly streamflow by MOSART at three stream gauge stations in the Missouri (upper), Mississippi (middle), and Ohio (bottom) river basins.



Observed (black) and simulated (red) monthly streamflow by MOSART at three stream gauge stations in the Missouri (upper), Mississippi (middle), and Ohio (bottom) river basins.

For evaluation of the energy consumption model (BEND) and electric consumption model (MELD), the calibrated models were used to simulate historical energy and electricity consumption. For BEND, historical weather data and historical building characteristics for 1990–2005 were used as inputs to simulate electricity consumption for selected utility regions and natural gas consumption for selected states. A similar approach is used for MELD. The above figure shows a comparison of estimated and actual electricity consumption for commercial, residential, and industrial regions. These results appeared in the publication the *Journal of Great Lakes Research*.

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

Martinus Oostrom

To improve our understanding of subsurface supercritical carbon dioxide ($scCO_2$) storage and caprock sealing efficiency, we have conducted 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 $scCO_2$-brine displacement processes to field applications.

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 main issues for any subsurface sequestration project are 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 $scCO_2$ storage capacity 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 completed a large number of micromodel experiments at supercritical conditions addressing the following scientific challenges:

- identify roles that porous medium properties, fluid properties, displacement characteristics (rate and volume), and wettability (including contact angle hysteresis) play during hydrodynamic trapping, when $scCO_2$ displaces brine, and during capillary trapping when brine displaces $scCO_2$
- experimentally and numerically study and improve understanding of the relationships between capillary pressure, fluid saturation, and relative permeability during pore-scale displacement processes.
- identify methods for upscaling pore-scale displacement processes to larger scales, such as the field scale.

To address these challenges, we designed and constructed two high-pressure systems for micromodel experimentation and a capability to obtain interfacial tension and contact angle data at supercritical conditions. We developed a method 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 also 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. 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*.

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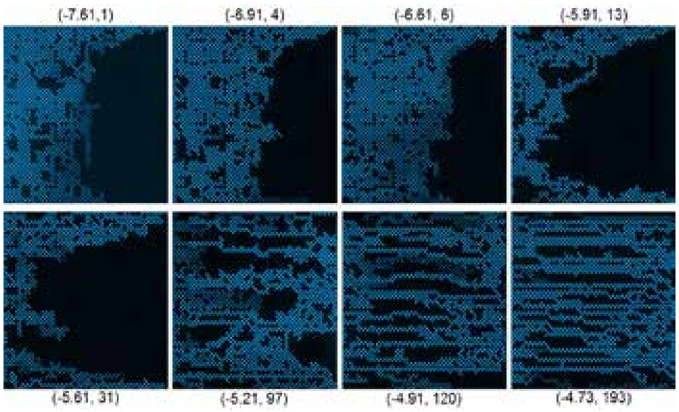
The micromodel experiments at high-pressure injection conditions conducted in FY 2011 were conducted with newly designed and constructed high-pressure cells equipped with high quality syringe pumps for accurate and precise fluid injections at constant pressure or at constant injection rate. Full control 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 CO_2-water displacements in a pore network micromodel with high and low permeability zones. Published in *Energy & Fluids*, results showed two distinctive fingering mechanisms: viscous and capillary. Other results published in *Environmental Science & Technology* reveal that due to the low viscosity ratio, unstable displacement occurred at all injection rates over two orders of magnitude. CO_2 displaced water only in the high permeability zone at low 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.



$scCO_2$ in a micromodel as a function of injection velocity. At low velocities, capillary fingers form. At very high velocities (e.g., near a well), displacement is in the form of viscous fingers.

Also in FY 2011, we developed and tested new methods to change the wettability of initial water-wet micromodels to oil wettability using treatment with silanes. The work provides a benchmark evaluation of surface wettability alteration by the silanization method, demonstrates a linear correlation between the resulting measured air-water and oil-water contact angles, and was featured on the cover of the journal *Langmuir*. 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 non-aqueous phase liquid migration in the subsurface.

During FY 2012, displacement experiments were conducted in intermediate and oil wet micromodels. Compared to displacement of brine in water-wet models, it was clearly demonstrated that imbibing $scCO_2$ was able to remove brine at much lower capillary pressures. This observation means that standard constitutive models for fluid retention and movement, as typically used in continuum simulators for water-wet sediments, are not appropriate. Instead, specified relations accounting for wettability changes are needed for accurate predictions of multifluid flow for porous media that are not water wet.

In addition, a method was proposed to improve predictions of $scCO_2$ imbibition in water wet model. The new method, using decoupled capillary pressure – saturation and relative permeability – saturation relations, as opposed to the typically employed fully coupled method, considerable improved predictions of displacement behavior in homogeneous and heterogeneous micromodels. The new method was published in the *Vadose Zone Journal*.

Finally, experiments were completed to study pore-scale entrapment of $scCO_2$ during displacement of brine. It was found that scale of entrapment occurred over multiple pores resulting in relative large disconnected blobs. Over time, the entrapped blobs shrink due to the relatively large dissolved CO_2 concentrations in brine.

Microscale Reconstruction of Biogeochemical Substrates Using Combined X-ray Tomography and Scanning Electron Microscopy

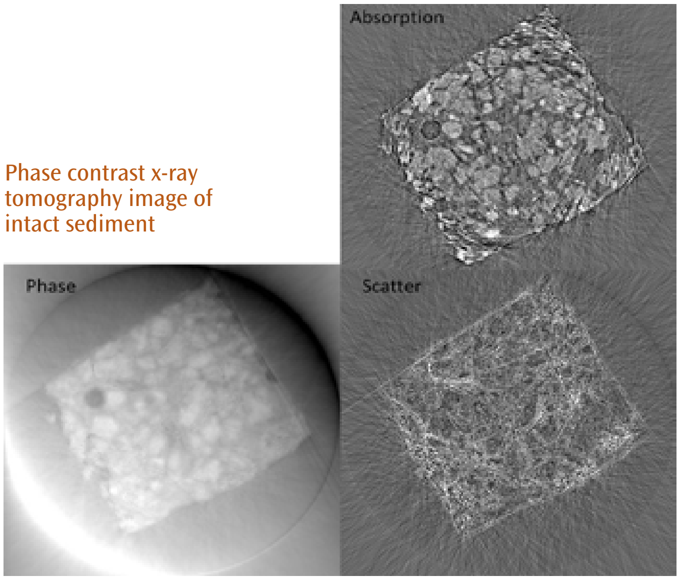
James P. McKinley

The collection of data in the form of sample imagery is a powerful tool used in many scientific investigations, and a family of scientific imaging tools is available to collect complimentary images of solid samples. The ability to combine images across imaging techniques and across imaging scales would represent a scientific tool that is more valuable than its individual parts.

The objective of this research is to combine and examine microscale images across multiple physical and chemical domains. Microscale imaging is ubiquitous in the sciences, and scientific images are common in in the popular press such as magazines and newspapers. The best known and most common images are photomicrographs, particularly scanning electron micrographs showing the invisible details of scientific samples; many of us have seen the scanning electron image of a fly's eye, for example. More specialized imagery includes representations of the composition of the sample, including variations in composition; the visualization of 2D spatial relationships among sample parts or subregions; the distribution of different crystalline properties within the sample; and the distribution of void space within a natural or manufactured material. Recently, the ability to produce x-ray tomograms (3D images analogous to CAT scans) has emerged as a significant tool.

Tomography relies on the differential ability of physical substances to absorb x-rays analogous to a medical x-ray, which maps absorption in two dimensions, with the additional computational reconstruction of absorption in three dimensions using multiple x-ray collections. The resultant images can be viewed either as rotatable solids or slices through the sample but do not include information on the specific compositions that are responsible for the absorption. This project will combine different types of electron microscope images (which do include compositional and crystal-phase information) with x-ray tomography images, to provide a detailed 3D image of solid samples that include chemical data.

This project began in mid-year FY 2012. Our approach was to begin by targeting natural samples with intact pore space and a complex, microscale assemblage of crystal phases with varying composition. If successful, our project could provide data for the quantification of fluid movement in micro-pores in nature and facilitate an understanding of chemical reactions that occur in the environment.



Phase contrast x-ray tomography image of intact sediment

Our approach is to collect x-ray and chemical data; to assimilate the data using software we develop and adapt; and to progress to more complex volumetric, multi-scale data as our experience and abilities evolve. We initially assembled intact sediment and soil samples, and began synthesizing artificial analogues using metal, mineral, and organic substances at different length scales. Tomographic images of the samples were collected; the samples will be physically sectioned and analyzed via electron microscopy methods; and the compositional data will be propagated into the tomographic solid using project-developed algorithms.

To investigate data collection across scales, we used the Advanced Photon Source at Argonne National Laboratory to collect tomographic images of portions of dissected samples using conventional and phase contrast methods at high resolution. We have begun evaluating the results using commercial and purpose-written software to determine the achievable optimized resolution of the EMSL tomography system and are investigating the incorporation of tomographic data across collection platforms. We successfully collected micro-scale tomograms using phase-contrast imaging (see figure); this method will aid in the detection and quantification of compositional regimes that are not readily observed using conventional tomographic methods.

In FY 2013, we will extend our efforts into the assimilation of scanning electron microscopy results and will begin exploring the computational methods and limitations to projecting chemical data into 3D x-ray space.

Non-destructive Challenge Measurements of Environmental Radiotracers

Robert Runkle

This project defined challenge measurements that have the potential to answer key questions in environmental science that range from the flow of water in ocean systems to the stability of carbon in soils. The identified measurements guide investments into novel, state-of-the-art radiation detection technology.

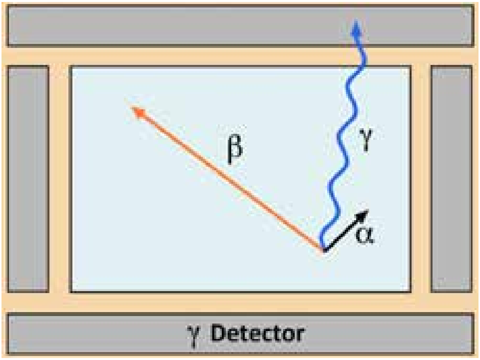
Environmental radioisotopes are commonly used as tracers of environmental processes. The first and most renowned example is ^{14}C, which was employed for dating the age of organic matter. Since the late 1940s when this method was developed, an expanding suite of environmental radioisotopes has been used as tracers of various processes, including groundwater movement (injection of water into aquifers and the flow of water through aquifers), mixing of ocean water, and sediment deposition. More generally, radiotracers can be used to describe the role of environmental radioisotopes, whose key value is that they are already present in the environment at useful concentrations and therefore do not affect the environmental processes under investigation. To be a valuable tool, the half-life of a radioisotope must be reasonably matched to the time horizon of the environmental process under study.

Recent investments in new technology produced measurement capabilities in PNNL's Shallow Underground Laboratory with potential to impact environmental science significantly through measuring environmental radioisotopes at extremely sensitive levels. The purpose of this study was to define a set of challenge measurements to be pursued under PNNL's ultra-sensitive nuclear measurements research program. We initially examined a large set of radioisotopes naturally present in the environment but quickly focused on a narrow set of opportunities, including radioisotopes in the hydrosphere, age dating of young groundwater, measurements of carbon stability in biomass, and radionuclides released from the Fukushima event in Japan.

The isotope ^{39}Ar presents the opportunity for age dating of subsurface water in the broad time frame from 50 to 1000 years. This analysis demonstrated that PNNL's specialized proportional counters offer the capability to measure reasonable sample sizes for ocean waters but not ice cores. In addition, there is considerable demand in the fundamental science community for assaying "ancient" argon that is needed to detect new phenomenon such as dark matter. Additionally, the isotope ^{22}Na has the potential for age dating of young ground waters. Despite PNNL's CASCADES array that presents a near-ideal tool for measuring signatures from ^{22}Na, there are apparently no ongoing measurements of this isotope due to complexities of analyzing young groundwater.

Dual measurements of the radioisotopes ^{14}C and ^{3}H have significant potential to inform the stability of carbon in soils. Deploying age-dating using these two isotopes provides two independent age dates that could result in an approach to measure the stability of different fractions of organic matter extracted from different soils. Successful measurements will provide unparalleled insights into the stability of different soil organic matter and contribute to new foundations for modeling soil carbon cycling processes. We recommend developing the necessary sample preparation and execute a demonstration measurement.

The emissions from the Fukushima nuclear power plant in Japan offer the potential to measure the migration of various radionuclides through environments, particularly through aquatic systems. Considerable interest will exist in coming years to measure trace concentrations of emissions that possess half-lives in a range of under 10 years. Currently, technology is not sensitive enough to access some of these isotopes. We recommend pursuing novel detection technologies with potential to exploit compound signatures, such as coincident emissions of various plutonium isotopes that allow separation from other elements like americium.



Schematic of a detector concept capable of exploiting a suite of signatures, often emitted simultaneously, from radioisotopes released during the Fukushima event. Harvesting various signatures is key to increasing detection system sensitivity.

This project defined a set of key challenge measurements that can be targeted by novel instrumentation. Future projects will develop the necessary chemical preparation technology and precision instrumentation required to execute the measurements with state-of-the-art technology in PNNL's Shallow Underground Laboratory.

PN12055/2456

Numerically Robust Climate Simulation Through Improved Interaction between Model Components

Hui Wan

The project will provide new methods for representing the interactions between atmospheric processes in numerical models. It will help to develop more robust and reliable tools for understanding and predicting climate change.

General circulation models (GCMs) that numerically solve the evolution equations of atmospheric motion have been used for more than 50 years as a fundamental tool in climate research. Recent progress in process studies, the fast growth of computing power, and the decision makers' need for detailed information of regional climate change all have motivated the current emphasis on high-resolution modeling. Complex processes such as aerosol lifecycle and cloud microphysics have been incorporated into global models, which dramatically broadens the spectrum of spatio-temporal scales that are explicitly represented by numerical methods. Although these processes interact strongly with each other and with the rest of the model, there is not yet an established theory or standard practice regarding the coupling technique.

By contrast, a number of studies have shown strong and worrisome sensitivities of model behavior to numerical details. The symptoms have revealed a major weakness in current climate models, which implies that great structural uncertainties exist in the simulated climate responses to anthropogenic forcing. The objective of this project is to reduce the numerical errors associated with component coupling in climate models. Through the development of new coupling methods, we aim at achieving a higher level of numerical and physical consistency between different processes as well as constraining artificial sensitivities in climate predictions.

During FY 2012, our investigations started with a literature search combined with review of model codes from various climate research institutions. It was determined that on the one hand, the hierarchical structure of GCMs – namely, the division of a model into a few major components that again contain several levels of sub-components – leads to a large number of complex interactions pathways. On the other hand, strong compensation and competition between processes are two situations that are both ubiquitous at different levels of this hierarchy as well as potentially susceptible to large numerical errors.

As the second step, a toy problem is established that describes the evolution equation of a gas species produced by chemical reactions in gas phase, and converted to liquid phase via condensation on pre-existing particles as well as formation of new particles. In this toy problem, production and condensation form a pair of strongly compensating processes, while condensation and new particle formation compete for available gas. Numerical convergence tests are performed to evaluate different coupling methods. Results show that the sequential operator splitting combined with explicit time stepping and long step size, a common choice in global climate models, leads to severe biases in the numerical solution. The use of analytical solution to a subsystem in the model and the application of implicit schemes for linear part of the evolution equation can significantly reduce the errors. Alternatively, explicit methods using dynamically determined sub-step size in combination with *a posteriori* error control can provide excellent trade-offs between accuracy and efficiency.

Outcomes of the literature review and results from the toy model have enabled us to refine the strategy and methodology of this project. The following research activities will focus on competing and compensating processes in cloud dynamics and microphysics that happen at time scales from seconds to hours. These are the newest components in current global GCMs, which have also been shown by numerous studies as a major source of uncertainty in current climate simulations. Throughout FY 2012, we performed a theoretical analysis of both the coupling technique and time integration methods used in the cloud microphysics parameterization in the Community Atmosphere Model (CAM), version 5. In terms of technical progress, a single column version of the model has been ported and validated on PNNL computers, which will be used as the main tool in the next steps.

For FY 2013, we will carry out a series of numerical simulations and data analysis with the single column model under different meteorological conditions to provide a detailed quantitative view of the cloud/rain water budget in CAM5. Compensating and competing processes will be identified in the budget analysis. Different methods will be used in sensitivity experiments to represent their interactions. The simulated cloud lifecycle and precipitation formation will be evaluated. Apart from the general goal of reducing numerical artifacts, the activities planned for FY 2013 will provide essential information about factors that determine the magnitude of aerosol indirect effect in CAM5. They are therefore expected to have a major impact on the cloud feedback and aerosol-precipitation-climate interaction studies carried out with this widely used climate model.

PN12059/2460

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

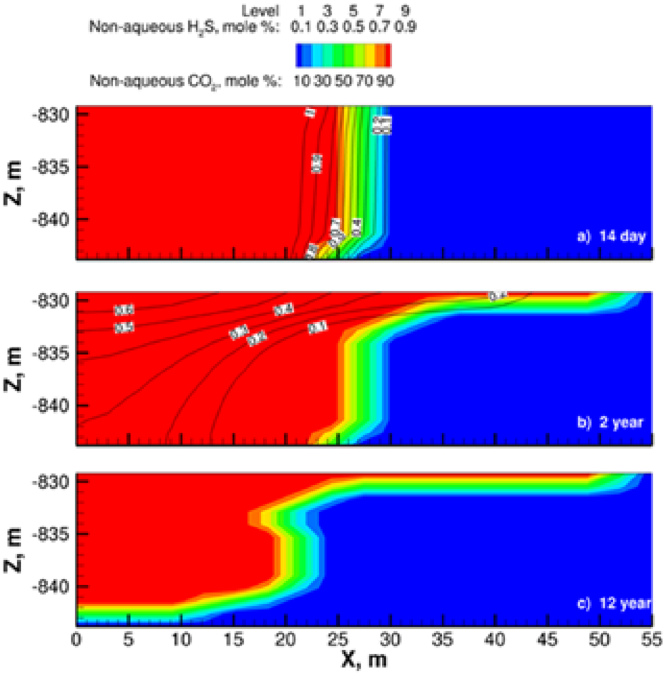
Diana H. Bacon

Using mineralogy of deep saline systems to co sequester NO_x and SO_x with CO_2 could significantly lower the cost of retrofitting coal-fired power plants for carbon sequestration. We are developing a simulator that will improve predictions of the impact of geologic co sequestration of CO_2, SO_x, and NO_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 is improving predictions of the impact of geologic co-sequestration of CO_2, SO_x, and NO_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-sequestration into 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 sequestration 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.



Co-injection of CO_2 and H_2S in a basalt formation. H_2S is consumed by mineral reactions more rapidly than CO_2.

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

PN10067/2309

flash equilibrium model, where phase composition is defined through fugacity equilibria. The new equation of state 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. 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 FY 2012, the component database was expanded to include 10 gases: CO_2, O_2, N_2, Ar, CH_4, C_2H_6, C_3H_8, C_4H_{10}, H_2S and SO_2. The predictions of the new Peng-Robinson equation of state in STOMP for component density, viscosity, enthalpy and thermal conductivity have been compared with the results predicted by higher order equations of state for all these gases in the National Institute of Standards and Testing database REFPROP 9. Predictions of the solubility of for each of these gases in pure water and brines have been compared to higher-order solubility models and experimental data. 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 as well as during phase changes. Mass and volumetric source terms have been implemented to simulate well injection. We added 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. In addition, we prepared a journal article on the development and application of the code to co-sequestration of CO_2 and H_2S in basalt.

For FY 2013, we will implement a parallel solution scheme using global arrays. We will prepare a journal article on application of the new model to field scale simulations of co-sequestration in various formations such as sandstone, dolomite, basalt and redbeds. Additional capabilities will be added to STOMP for problems involving the injection of CO_2 into partially depleted petroleum reservoirs. The new equation of state will also be founded on a cubic formulation, but will additionally include a nonaqueous liquid phase.

Quantitative Framework Development to Support Effective Monitoring for Metal and Radionuclide Contamination

Michael J. Truex

> ***Many methods for subsurface remediation mitigate exposure risk but leave contaminants in place. In these cases, especially for contaminants such as metals that do not degrade and radionuclides that decay slowly, effective monitoring approaches are necessary to verify continued remedy performance and human health/environment protection.***

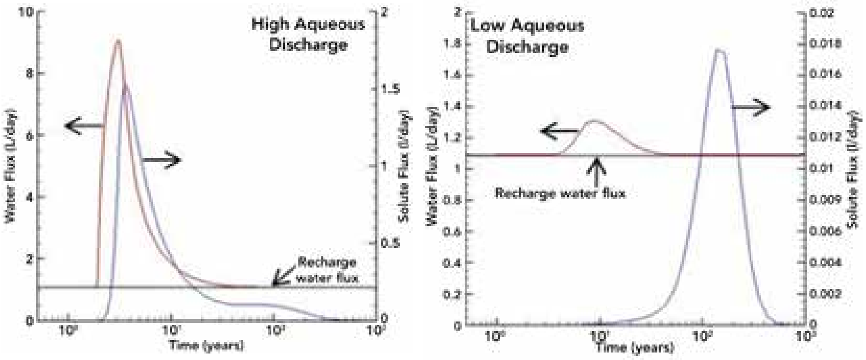
Most traditional monitoring approaches focus on point-based compliance monitoring and yield contaminant concentrations at selected locations at snapshots in time. These data alone may be insufficient to evaluate remedy performance. Recently, the need for expanded approaches to monitoring design has been recognized to support effective inferences about contaminant plume conditions and potential future contaminant movement. The use of numerical simulation analyses in conjunction with a conceptual model provides the ability to quantify the role of specific features and processes in controlling contaminant fate and transport and in meeting remediation goals.

The quantitative framework developed in this project addresses a current challenge in the monitoring technique development and selection: understanding how monitoring data provided by a candidate technique (e.g., type, sensitivity, and resolution) can be used for interpreting contaminant fate and transport. The quantitative framework for monitoring design and interpretation is intended to support advancement of lines-of-evidence systems-based monitoring approaches that provide a more cost-effective approach to long-term site management than conventional monitoring approaches.

Numerical models were configured for conceptual model scenarios, including several types of imposed initial contamination conditions representative of key DOE issues. The focus in FY 2012 was on contaminants residing in the vadose zone that have potential to migrate downward and contaminate groundwater. These contaminants pose a potential long-term liability because vadose zone migration is slow and may generate groundwater issues for years after initial waste disposal. The goal of numeric simulations was to identify monitoring targets in the vadose zone with appropriate resolution for use in interpreting or predicting contaminant mass discharge to groundwater and/or contaminant concentration at a compliance location. Key findings of the simulations are summarized below.

- The ability to monitor a perturbation in moisture content caused by an aqueous waste discharge is a function of the relative size of the waste discharge and the vadose zone thickness. The quantitative results from these simulations have important implications in relation to the resolution and sensitivity of vadose zone moisture monitoring.
- Over time, recharge rate becomes the controlling factor in contaminated moisture migration in the vadose zone. In most cases, except for large disposal volumes relative to the vadose zone size, the majority of contaminant flux to groundwater occurs under recharge-driven moisture flux conditions due to dissipation of elevated moisture content and dispersion of contaminants caused by unsaturated flow processes. Thus, monitoring of recharge conditions is critical to evaluating contaminant flux to groundwater.
- The impact of low permeability layers on water and contaminant migration is a function of moisture content magnitude change induced by waste discharge. For relatively low moisture content change, low permeability layers have little impact on vertical migration; for higher, low permeability layers cause lateral spreading and/or perching conditions, where the contaminant migration rate to groundwater can be significantly controlled by layers until moisture reverts to recharge-driven conditions. Thus, specific monitoring of low-permeability layers is primarily diagnostic under high, not low, waste-discharge conditions.

Future efforts will focus on completing a technical report describing implications of the quantitative simulation results on vadose zone monitoring and related simulations of groundwater plume dynamics. Additional simulations will be conducted, including an assessment of groundwater-surface water interfaces.



Simulated water and solute flux from the vadose zone to groundwater. Even non-sorbing contaminants migrate slower than the added water pulse and, as discharge volume decreases, more of the contaminant discharge to groundwater occurs under recharge-driven conditions.

PN12066/2467

Simultaneous ^{14}C and T Dating: A Case Study Using Soil Organic Matter

James J. Moran

> ***We are developing high-resolution methods for age-dating organic compounds. Applying these methods to soil samples, we will better understand how soil contributes to global carbon cycling and to what extent different carbon-containing molecules can be stored in soils.***

Typical sample preparation techniques preclude simultaneous analysis of both 14-carbon (^{14}C) and tritium (T). For instance, ^{14}C analysis by accelerator mass spectrometry (AMS) requires conversion of an organic sample to either CO_2 or graphite, forcing T analysis on the same sample to be analyzed separately. In contrast to AMS, analysis by the Ultra-Low-Background Proportional Counter (ULBPC), which is developed and housed at PNNL and provides a capability for dual isotope measurements on single compounds, requires only that a sample be converted to a volatile gas (with higher sensitivity expected from gases with low electronegativity). A unique capability exists for simultaneous ^{14}C and T analysis whenever a sample can be quantitatively converted from its native, complex form to a suitable simplified gas form.

A prime example highlighting the power of simultaneous co-measurement of ^{14}C and T is within soil organic carbon. Studies show that an increasing concentration of atmospheric CO_2 and other C- and N-based greenhouse gases are driving global climate change. Heightened concern over atmospheric carbon content, combined with the sheer size of the terrestrial soil carbon pool, make understanding the carbon exchange between soil and atmosphere crucial to constraining the overall global carbon cycle. Despite recent attention to this issue, however, gaps remain in our understanding of the fate of organic carbon in soil: it is uncertain whether carbon recalcitrance is controlled by chemical structure, physical protection, or a combination of both factors. Given that soils are continuously bathed with water, dual dating of ^{14}C and T could identify how dynamic physically protected carbon is and whether this is physical or chemical protection (i.e., completely controlled by the nature of the chemical structure or more independent of the chemical form and more dependent on impact from location in the soil). T could also be used to identify pool turnover rates in seemingly persistent carbon pools. This information would powerfully enhance our current understanding of carbon stability in soils and in turn improve current modeling efforts and our ability to predict the long-term disposition of carbon in soils.

We are developing a more sensitive method for simultaneously measuring the age of soil organic compounds using these ^{14}C and T dating approaches. As noted, previous work with soil organic carbon assessed the ^{14}C age of soil organic materials, but this by itself only reveals the age of the carbon in the soil and may not capture molecular processing through microbial or abiogenic activity. With this dual-isotope method, we will have enhanced the resolution for looking at specific bond-breaking within these organic molecules, and we should be able to distinguish very old carbon locked in a stable chemical molecule, versus old carbon that has been actively shuttled between the different components within the soil.

Throughout the world, soil offers a tremendous storage capacity for organic carbon. With heightened concern over carbon storage and allocation between different systems (soil, atmosphere, aqueous, etc.), understanding which organic compounds are stable in soil and represent a lasting form of sequestration is critical. In addition, central to the scientific objective of organic molecule stability in soils is a method for making simultaneous ^{14}C and T age dates on organic molecules. Traditional approaches require separate preparative steps and measurements for each date, requiring higher sample amounts and additional processing. We seek to develop a system to process organic compounds into a molecule suitable for dual isotope dating while not altering the initial isotope content.

Specifically, our work in FY 2012 commenced with our research team's main focus to identify the most suitable methods for converting soil organic material into a chemical form that is appropriate for isotope measurement using a proportional counter. We settled on a two-phased approach, where samples are first combusted to CO_2 and water, with these products then used as a feedstock for synthesizing methane. The methane is purified and then directly used for an isotope analysis. Refining this kind of chemical conversion method is crucial to this project's goal of making simultaneous dual isotope dates on soil organic carbon.

During FY 2013, we intend to focus first on assessing the above-described method to ensure that the isotope content of the methane product matches that of the starting material (as measured specifically by an orthogonal method). Next, we will begin a series of steps to extract, identify, and separate different compounds from a local, organically rich soil. In short, we hope to demonstrate the variable stability of different classes of soil carbon based either on the chemical structure of the compounds or the location of the compounds within the soil.

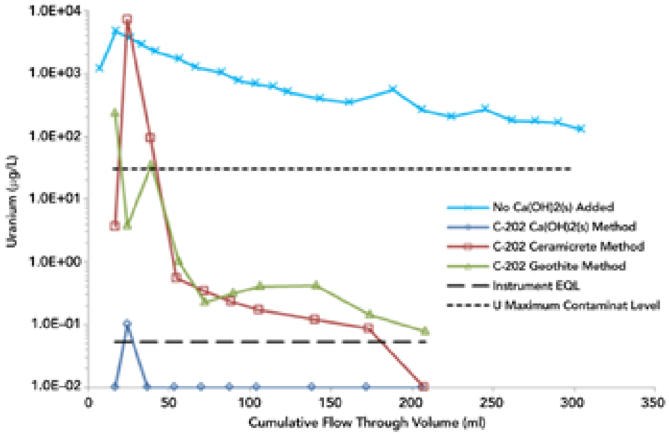
PN12071/2472

Tank Residual Waste Stabilization to Reduce Contaminant Release

Kirk J. Cantrell

We are developing and demonstrating a science-based approach for stabilizing contaminant release from tank residual waste that can be used to determine waste retrieval endpoints that are risk-based rather than based on an arbitrary volume goal.

Recent work at PNNL has demonstrated that the development of the scientifically based mechanistic release model is critical to understanding contaminant release from post-retrieved tank waste residuals. For example, studies about the uranium release from Hanford's C-200 series tanks have shown that in spite of the 99% retrieval goal being achieved, uranium release from the residual waste is still expected to be over three orders of magnitude above the maximum contaminant level (MCL). The focus of this project is to demonstrate that chemical additives can be used to stabilize the residual tank wastes post-retrieval, greatly reducing contaminant release (in particular, technetium [Tc], chromium [Cr], and U). This innovative approach has the potential to revolutionize Hanford's tank retrieval process by allowing larger volumes of residual waste to be left in tanks, while providing an acceptably low level of risk with respect to contaminant release that is protective of the environment as well as human health. Such an approach could enable DOE to realize significant cost savings ($10 million or more per tank) through streamlined retrieval and closure operations. With more than 140 single-shell tanks waiting to be retrieved at Hanford alone, total cost savings could be in excess of $1 billion.



Experimental results for uranium, demonstrating the effectiveness of three tank waste stabilization methods relative to grout only (simulated, with no solid $Ca[OH]_2$ added).

With the aid of a thermodynamic solubility release model developed to predict future uranium release from tank residuals, a simple and inexpensive method was designed to render uranium insoluble within the residual waste through the addition of a small layer of lime ($Ca[OH]_2$) on top of the tank residuals prior to closure. In addition, it is possible to immobilize reduced Tc(IV) and Cr(III) in insoluble iron oxide mineral phases through a co-precipitation process that isolates reduced Tc(IV) and Cr(III) from the pore water and prevents their reoxidation to TcO_4^- and CrO_4^{2-}. A third approach was to form stable phosphate bonded ceramics to sequester contaminants. This type of process can be used as part of a risk-based closure strategy to demonstrate that a greater volume of waste can be left in the tanks while reducing actual overall risk levels.

Three treatment methods were tested: a $Ca(OH)_2$ addition, a ferrous iron/goethite treatment method, and an *in situ* ceramicrete waste form based on chemically bonded phosphate ceramics. These approaches rely on chemical reduction and the formation of highly insoluble forms of the contaminants of concern. Results have demonstrated that for all three methods, the release of the three most significant contaminants of concern from tank residual wastes can be dramatically reduced, compared to contact with simulated grout porewater. For uranium specifically, all three treatments methods reduced the leachable uranium concentrations well over three orders of magnitude (refer to the figure). In the case of uranium and technetium, the release concentrations were well below their respective MCLs for the wastes tested. For two of the three wastes tested, chromium release concentrations were also below the MCL. For the third waste sample, chromium release was above the MCL, but it was considerably reduced relative to the untreated waste.

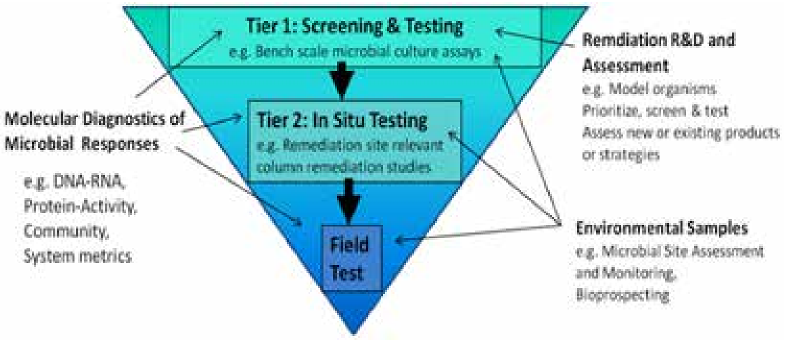
Work will be ongoing throughout the next fiscal year to identify the specific mechanisms responsible for reducing these contaminant releases through various characterization techniques and geochemical modeling that will be performed after testing is complete. Results of this work will be disseminated in a peer-reviewed journal article in FY 2013.

Translating Microbial Ecology Advances into Applied Tools for Remediation and Monitoring

Fred A. Tilton

Few regulatory standards assess beneficial or adverse outcomes driven by microbial communities that could arise from subsurface remedial activities. This potential costly "blind-spot" in management and monitoring of contaminated sites could be addressed with tools that provide predictive, defensible benchmarks to assess risk quantitatively.

Microbial life in the subsurface has become widely recognized and studied for its potential usefulness or relevance at many DOE waste sites. Consequently, DOE and other government agency investments have gone toward understanding and controlling microbial process at the molecular level (DNA-RNA-Protein-System). As the manipulation or control of microbial communities for the purposes of remedial activities matures, developed molecular tools will need to be standardized and utilized within an efficient, agreed-upon framework.



Microbial-remediation assessment framework: tools, strategies, and assessments for microbial-remediation interactions.

In the first phase of development, we derived a tiered testing framework to incorporate molecular technologies and assess microbial contributions to remediation outcomes. As proof-of-concept, we used a tiered approach with model organisms and native communities from deep vadose zone sediments to assess potential microbial ramifications of subsurface remediation technologies under development. This work developed low-cost, relevant, rapid metrics of value to remediation and management decisions.

We exposed *Shewanella oneidensis* cultures to graded concentrations of foam-based amendment components to assess microbial response potential as a robust, rapid, low-cost Tier 1 screen. Most resulted in a significant response (death/growth) relative to controls; however, sodium dodecylsulfate (SDS) presented the greatest potential, given a significant stimulation of growth rates at concentrations found in proposed foam blends. Other constituents showed significant bactericidal properties, albeit at unrealistic levels for field deployment. Using a model organism of significance to metal/radionuclide remediation with well described and malleable genetics, we established a rapid, robust bench-top screening system that is adaptable to state-of-the-art molecular tools.

With significant microbial responses and predicted relative risks, we moved SDS and cocamidopropyl betaine (CAPB) to Tier 2 testing. We wanted to address whether the 200 Area deep vadose native microbial communities (DNA isolated/identified in 2010) would elicit similar responses under conditions mimicking remediation activities. Consequently, we exposed sediments from the 200 Area deep vadose zone depths (with and without microbial stimulation) to solutions containing one of the amendment components in columns at flow rates of ~200 uL/hr. The marginal toxic response to CAPB in our Tier 1 screen was not observed in native 200 Area sediments. Consequently, its bactericidal properties may have marginal impact in "sterilizing" deep vadose zone sediments. The growth from SDS exposure was replicated in native sediments but at lower rates. We observed a congruency of evidence, which demonstrated that many amendment components induce relevant microbial responses that could impact remediation success. Future formulations will be informed by these data, which highlight the presence of active, malleable microbial communities in the deep vadose zone.

Site-specific remediation decisions will prove costly and ineffective without a framework to prioritize, screen, and evaluate microbial and remediation interactions. In its first phase, this project demonstrated a novel opportunity to use microbial-amendment metrics in amendment pre-testing to "build-in" controlled responses of subsurface microbial communities. This testing has wide applicability beyond subsurface remediation and radionuclide stabilization as an integration of concepts in toxicological risk assessment, geochemical testing, and microbiology. This study provides a framework by which to incorporate novel tools (such as PCR arrays) and approaches into a standardized regulatory framework.

PN12077/2478

Uncertainty Quantification and Risk Assessment Pipeline for Carbon Sequestration

Guang Lin

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 and 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 formations 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 the 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. Predictive modeling of multi-scale and multi-physics 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 existing state-of-the-art tools as much as possible 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, reduced-order model development, parameter calibration/optimization, 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.

During FY 2011, we developed a preliminary uncertainty quantification framework for studying the effect of reservoir spatial heterogeneity on CO_2 sequestration. Continuing into FY 2012, we developed a prototype UQ and risk assessment workflow pipeline based on Velo (A Knowledge Management Framework for Modeling and Simulation) by coupling input uncertainty characterization, sampling generation, ensemble sampling simulation runs at supercomputer centers, analyzing ensemble results and visualizing the statistical results together. We developed a demonstration package that can automatically generate ensembles 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 Velo-based workflow for the uncertainty quantification of carbon sequestration simulations. The developed workflow prototype laid a solid cornerstone for developing a UQ and risk assessment pipeline for the carbon sequestration simulations for testing performed during this current FY.

For a UQ study on the impact of uncertainty and heterogeneity of spatial permeability field on the CO_2 plume radius propagation, we employed the quasi-Monte Carlo and probabilistic collocation methods in FY 2012 to generate permeability sampling inputs for eSTOMP and conducted the ensemble runs using eSTOMP on large-scale supercomputer centers. Additionally, we developed a response surface method that can adaptively guide the sampling location and greatly reduce the computational cost in ensemble runs to study the relationship between the uncertainty and heterogeneity of spatial permeability field on the CO_2 plume radius. These results were recorded and submitted to the journal *Mathematical Geosciences*. Further, we explored effects of data quality, data worth, and redundancy of CO_2 saturation data on injection reservoir characterization through PEST inversion, reporting our results to *Greenhouse Gases*: *Science and Technology*. Further outcomes from this past year included the creation of research quality codes for building adaptive response surface and developing efficient sampling method to reduce the computational demand for uncertainty quantification. We also worked with another project, where we conducted the model comparison and uncertainty quantification of the SIMSEQ data sets. We presented these results collectively at both the American Geophysical Union Fall Meeting and the 11th Annual Conference on Carbon Capture Utilization & Sequestration.

For FY 2013, we will perform the uncertainty analyses of CO_2 plume expansion in reservoirs and wellbore leakage in aquifers. We will continue to develop the UQ and risk assessment workflow pipeline and integrate more UQ components into the pipeline. Finally, we will develop efficient UQ and model calibration methods and software for results in top journal publications.

PN11077/2399

Understanding the Sources and Consequences of Uncertainties

Richard H. Moss

Understanding the sources and consequences of uncertainty in regional models results is crucial for robust adaptation and mitigation decisions. This project is developing and demonstrating rigorous and tractable methods for uncertainty characterization (including uncertainty quantification and propagation) in the integrated Regional Earth System Model (iRESM) framework. Research results are informing iRESM model development, the design of numerical experiments, and methods for analyzing uncertainty and communicating results to decision makers.

The iRESM modeling framework aims to project climate change and adaptation impacts and mitigation options by modeling interactions between human and earth systems (e.g., electricity production, streamflow quantity, temperature affecting cooling water availability). These interactions occur within and between individual sub-national geographic regions nested in national and global changes in the same systems. In addition, iRESM is intended to provide policy-relevant insights 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 fidelity and policy relevance, uncertainty in model results must be characterized in a computationally feasible, transparent, and practicable manner using a variety of methods.

In FY 2011, this project developed a 10-step uncertainty characterization (UC) process predicated on conducting 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., the bases upon which alternatives are compared) 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 2012, project research focused on initiating a demonstration of the UC process developed in FY 2011 by another project and analyzing approaches to address run time requirements of uncertainty propagation for the iRESM framework. Results of these efforts are documented and summarized below.

Demonstration of the UC process. The project utilized the results of iRESM research into stakeholder decision support needs in the pilot region (US Midwest) to provide a decision context for the demonstration. The team drew information from an analysis in the literature about climate mitigation and adaptation questions asked by subnational-level decision makers and focused on 14 upper Midwest states. Among other issues, stakeholders were interested in the roles of building energy codes and equipment energy efficiency as a means for adapting to or mitigating climate change. The team took as its model decision at what rate states might implement more aggressive building energy codes and residential and commercial appliance and equipment standards. The team considered three cases: "frozen technology" (no change), a 50% reduction in energy use by 2050, and an 80% reduction in building energy use by 2050. Different stakeholder groups in the 14-state region had different decision criteria; for the purposes of the demonstration, the team focused on energy consumption, greenhouse gas emissions, and operating costs per square meter (including equipment depreciation, energy charges, and carbon price). The uncertainty characterization focused on the effects of input quantification and model skill/model completeness issues. Under input quantification, the team considered population growth and the rate of growth of economic output per worker. As a first step under model skill and completeness, the team considered uncertainty in future emissions with the Intergovernmental Panel on Climate Change's A2 and B1 emissions cases, and three general circulation models (incorporating uncertainty in regional climate response, given an emissions scenario).

Using iRESM's regional integrated assessment model, RGCAM, the team analyzed the sensitivity of energy consumption, greenhouse gas emissions, and the operating costs per square meter to the four sources of uncertainty

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described above. The team generated RGCAM results for all 50 states from 2005 to 2095 following a 162 combination full factorial design: 3 regional standards scenarios × 2 national/emissions pathways × 3 population scenarios × 3 GDP growth rates × 3 climate models. The team analyzed this dataset with both full factorial and second-order fractional factorial models, the latter featuring the 5 main effects and 10 second-order pairwise interactions. The fractional factorial analyses show how the amount of total variance in each decision criterion (energy, carbon emissions, and cost) is explained by the various sources of uncertainty and thus indicate the important input uncertainties to analyze in an uncertainty propagation. For example, the analyses of variance (ANOVA) of the fractional factorial models show that the 5 main effects and 10 second-order interactions explain over 99.9 percent of the squared error in costs of residential and commercial building services in Wisconsin in 2050 and 2095 for the 162 combinations (see table). Only 3 model terms are necessary to explain over 98 percent. Parallel ANOVA analyses for the energy consumption and carbon emissions criteria, and for other states, show that this explanation of impact is unique to the policy experiment, decision criterion, region, and time step but is easily replicable for other conditions (models, experiments, and decision criteria) and can quickly identify the sensitive inputs in each case. The ANOVAs also show that though a specific RGCAM output can be summarized by a parsimonious factorial model, distinct RGCAM outputs required distinct factorial models, with the implication that more runs would be required to characterize RGCAM uncertainty than one is lead to believe by the fit of one fractional factorial model to one output.

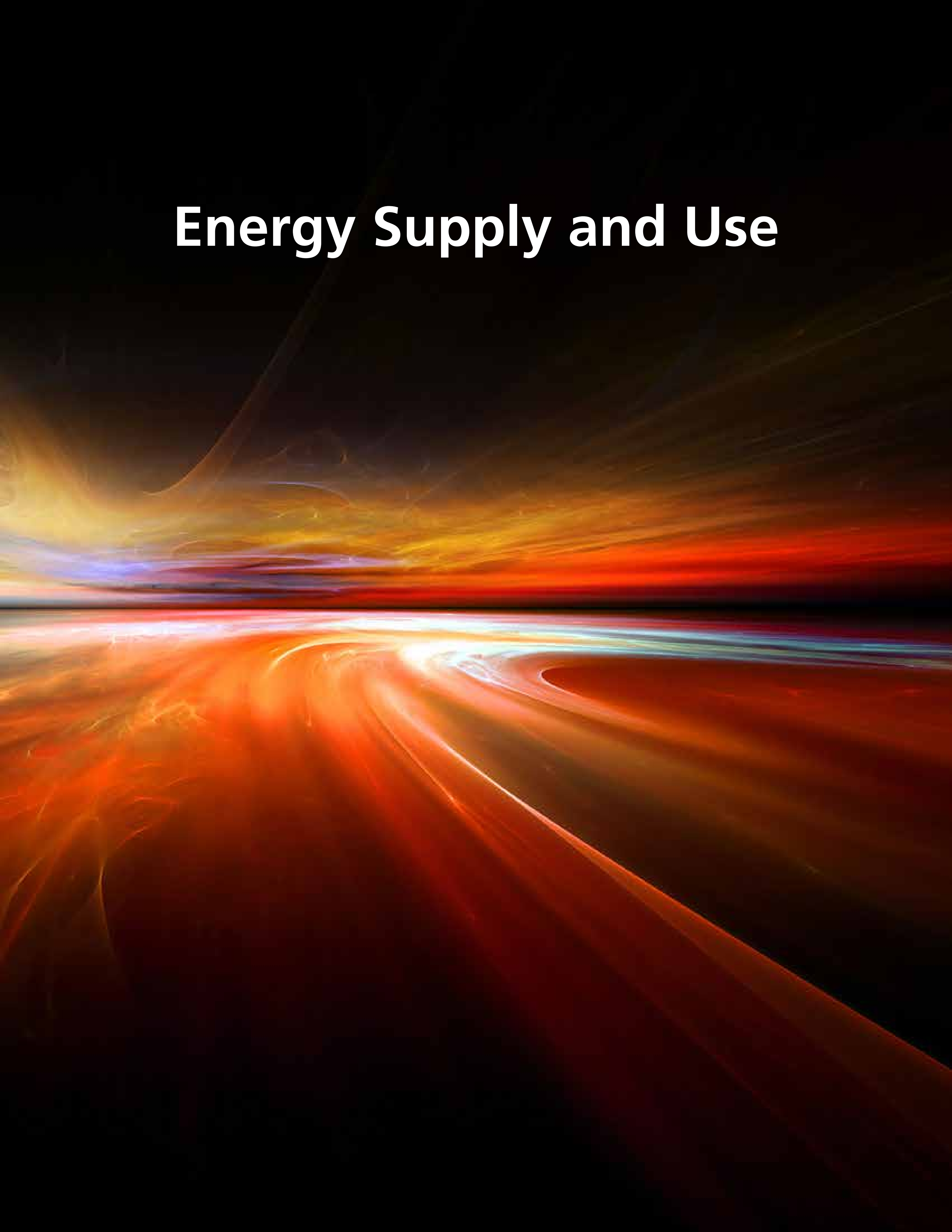
FractFact Model Term	Wisconsin Residential		Wisconsin Commercial	
	2050	2095	2050	2095
Standards	7.0	31.4	18.5	40.9
Conc Pathway	7.6	33.4	12.2	25.7
Climate Model	0.0	0.0	0.0	0.0
GDP	84.6	33.8	68.3	31.9
Population	0.0	0.0	0.1	0.1
Standards: Conc Pathway	0.3	0.4	0.2	0.3
Standards: Climate Model	0.0	0.0	0.0	0.0
Standards: GDP	0.4	0.9	0.4	1.0
Standards: Population	0.0	0.0	0.0	0.0
Conc Pathway: Climate Model	0.0	0.0	0.0	0.0
Conc Pathway: GDP	0.1	0.0	0.1	0.1
Conc Pathway: Population	0.0	0.0	0.1	0.0
Climate Model: GDP	0.0	0.0	0.0	0.0
Climate Model:Population	0.0	0.0	0.0	0.0
GDP: Population	0.0	0.0	0.0	0.0
All 15 Terms	100.0	99.9	99.9	100.0
Highlighted Terms	99.2	98.6	99.0	99.5

Percent mean square error of residential building services costs per m^2 of floorspace explained by a fractional factorial model of predicted costs for Wisconsin.

Run-time analysis. From 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 done 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. During FY 2012, the team investigated several response surface approximation methods to create a mathematical model of the propagation of uncertainty. The team examined two powerful non-linear multivariate regression approaches to optimize the response: artificial neural networks (ANN) and multivariate adaptive regression splines (MARS). With only a few training datasets, the methods establish the response relationships between the dependent variables of interest (outputs) and multiple independent variables (inputs) and can be used in predicting outputs for expensive high-fidelity simulations or predicting future events for a time-evolved system.

This project concludes in FY 2012. Work that builds on the results of this project will continue in FY 2013 other projects, which will include work to broaden the sensitivity analysis to other decision criteria and experiments with RGCAM, use sensitivity analysis to identify critical model couplings with the other iRESM models, implement strategies for quantifying the uncertainties identified in the sensitivity analyses, and develop the tools and methods needed to address uncertainty propagation across the iRESM framework.

Energy Supply and Use

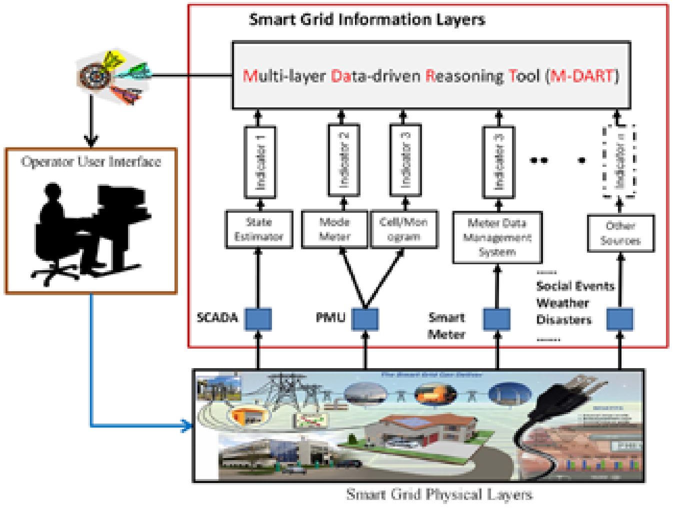


A Multi-Layer Data-Driven Advanced Reasoning Tool for Smart Grid Integrated Information Systems

Ning Lu

The objective of this research is to develop a decision support tool – Multi-layer, Data-driven Advanced Reasoning Tool (M-DART) – for improved power system operation.

Today's information management in power grid operation tools mainly follow a stovepipe process. Each sensor network produces its own domain-specific data (e.g., phasor measurement unit [PMU], supervisory control and data acquisition [SCADA], and smart meter measurements), and each data source is processed by domain-specific tool sets. The outputs are then presented to grid operators responsible for making decisions. Isolated data processing mechanisms focusing on individual data domains may not be able to reveal the root cause of failures or accidents and assess their impact to plan for action in a timely manner. As the number of different data sources increases, the possible action options increase exponentially; therefore, it is a significant cognitive challenge to the human operator who is stressed to analyze these relationships and/or draw on relevant past experience.



Conceptual illustration of the M-DART architecture

The current practice in the power grid operations community is to run massive offline analyses to derive model-based guidelines for online real-time operations. However, because power system components and configurations change in real time, it is hard for offline model-based analyses to maintain relevance and effectiveness. With the added problem of stove-piping of data, the resultant increased volume and complexity of data will only exacerbate human performance difficulties and lead to information overload and degraded decision making.

In view of these challenges, M-DART will investigate existing reasoning tools and apply two best performed tools to perform higher-level reasoning (cross-correlate and examine different data sources to assess anomalies, infer root causes, and anneal data into actionable information) to identify highest priority problems for the human decision maker to address. By summarizing results obtained from different reasoning methodologies, M-DART focuses on more accurate early detection of emerging power system events and identifies highest priority actions for the human decision maker to address. M-DART represents a significant advancement over today's grid monitoring technologies that apply offline analyses to derive model-based guidelines for online real-time operations and use isolated data processing mechanisms focusing on individual data domains.

In FY 2012, the efforts were focused on the development of M-DART. Two prototypes were implemented, one of which characterized the PMU data quality. Another M-DART tool is the Columnar Hierarchical Auto-associative Memory Processing in Ontological Networks (CHAMPION), a semantic-graph-based domain-independent reasoning system. CHAMPION can integrate multiple data types and sources. The hierarchy of reasoning components divides the analysis into portions of a potentially large semantic graph to facilitate scalability. To illustrate the reasoning process, assume we have monitor data from network measurements from PMU, SCADA, or smart meter data records. CHAMPION process the input and deposit appropriately formatted data into Working Memory, which is implemented as a semantic graph. The CHAMPION processors comprise a hierarchy of reasoners that is configured by ontologies that determine the processors' analysis of input data. Through this analysis, the reasoners construct and enlarge the semantic graph.

Also during FY 2012, we successfully collected 48-hour data from our industry partner, ISO-New England. The data analyzed includes 31 PMU channels within 6 PMU groups, SCADA data and state estimator. One example of analysis result is shown in the figure, which indicates the quality performance of PMU installed in different areas can vary significantly. Collectively, the results of our work

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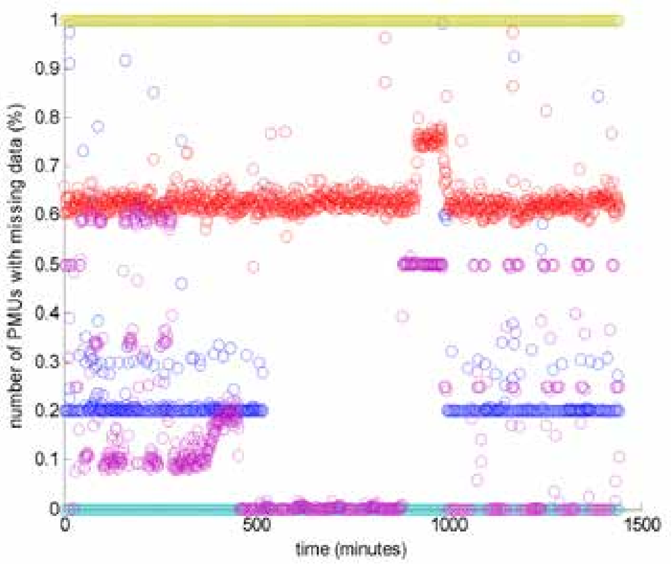
during this year were presented at two IEEE conferences. Future work will continue to explore the implication of PMU data quality for the grid's operations.

For FY 2013, we will continue to develop ontologies representing expert knowledge to drive the CHAMPION reasoning system and proceed with integrating advanced reasoned with selected PNNL tools. In addition, we will continue to develop further in-depth the appropriate test scenarios to exercise the reasoning system and select tools and create the required interfaces/displays for the integrated system. Additional coordination with industry partners is also forthcoming during the next and future fiscal years..



Analysis result of PMU data quality. Each color represents PMU data corruption ratio for different regions.

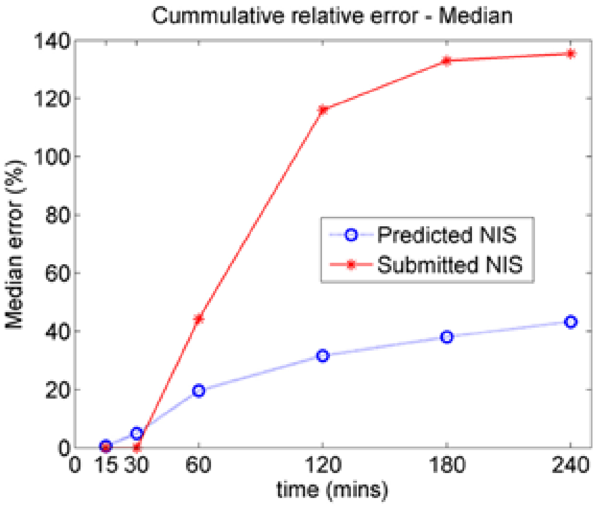
A Statistical State Prediction Methodology to Improve Reliability and Efficiency of Power System Operation

Ning Zhou

Motivated by challenges of increasing uncertainty and variation brought by the high penetration of renewable generation to power system operations, we are developing a short-term prediction and uncertainty quantification methodology at grid level to enable well-informed proactive operations, which will 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 in the range of 0.5–5 minutes, current state estimators can only provide power grid status in the past. Operation decisions based on these 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 are developing 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.



The comparison of prediction accuracy of NIS between our prediction method and the submitted values.

In FY 2011, we developed five forecasting methods and applied them for predicting Net Interchange Schedule (NIS) from a set of field measurement data. In FY 2012, a new set of field data measurement data of about one year were obtained to test the applicability and generalization of the prediction methods. The prediction methods are applied to the new data set and additional auxiliary inputs (e.g., season, time of day, day of week, trends) are included to improve their performance. The comparison shows improved prediction accuracy over the submitted NIS (see figure). We also explored several ensemble approaches (including bagging and stacking, incremental learning) to combine the prediction results from several prediction method to improve the accuracy of the prediction.

Also in FY 2011, we developed a novel efficient uncertainty quantification algorithm (probabilistic collocation) and performed an initial study on a sensitivity based adaptive sampling method to propagate the uncertainty of using an IEEE 30-bus system. In FY 2012, the sensitivity based adaptive sampling method was refined and compared with Monte-Carlo, linearization, and collocation methods based on the IEEE 30-bus model. To achieve same level of accuracy, the sensitivity based adaptive sampling method used 61 sampling points, while the collocation method needs 301 sampling points and the Monte Carlo method requires 10,000 sampling points. Errors using the linearization method were large compared to the other methods. The study shows the significant advantage of the sensitivity-based adaptive sampling method for reducing the computational complexity required to achieve a certain level of accuracy.

The goal of FY 2013 work is to position PNNL at the leading edge of power system prediction through improving the performance of the prediction methods and building demo cases. Based on the work in FY 2012, we will enhance the performance of prediction methods through improving the ensemble approach for prediction. We also plan to integrate the error quantification methods with uncertainty propagation methods. A demonstration case will be built with integrated prediction and uncertainty quantification methods to show the prediction results using real-world data.

PN11004/2326

Cooperative Control of Distributed Energy Resources for Grid Support

Marcelo A. Elizondo

This project develops optimal control coordination strategies for distributed energy resources (DER) to achieve local and global objectives for grid support under normal and stressed conditions. Centralized and decentralized control strategies are designed to optimally coordinate the actions of the DERs.

Controllable distributed energy resources (C-DERs) such as demand response, energy storage, electric vehicles, and distributed generation have the potential to contribute when integrating large-scale renewable generation. The DERs can also help the grid under stressed conditions. However, their coordination and control strategies are challenging because of additional variability and uncertainty from increased renewable penetration. This project addresses this problem by developing optimal control algorithms and coordination strategies for C-DERs to deal with uncertainty and variability from local renewable distributed energy resources (R-DERs). The project also develops control algorithms for arming and coordinating decentralized immediate response of DERs to help the grid during stressed conditions.

Microgrid configurations (isolated and grid-connected) with high penetration of R-DERs and C-DERs are used as example applications for testing the proposed strategies. The control algorithms developed in this project are aimed at removing the technical barriers of operating a power system with high penetration of DERs. They will also be at the heart of distribution energy management systems (DMS) in order to operate a portion of the distribution network or an isolated microgrid. During the past year, this work resulted in a total of four peer-reviewed publications.

Centralized control algorithms are proposed to coordinate energy storage and diesel generators to maximize wind penetration while maintaining system economics and normal operation performance. The goals of the optimization problem are to minimize fuel costs and maximize the utilization of wind while considering equipment life of generators and energy storage. Model predictive control (MPC) is used to solve a look-ahead dispatch optimization problem. In this approach and at every step, a finite horizon optimal control problem is solved using feedback from the system. The control action at each step is computed on-line rather than using a pre-computed, off-line, control law. In this manner, MPC is considered closed loop and has the ability to compensate for additional uncertainty and variability caused by high penetration of renewable energy resources.

A simulation model of a microgrid operating in islanded operation was developed in a commercial power system simulation package DIgSILENT. It was built specifically using the IEEE 34 node distribution feeder, including C-DERs (storage, diesel generators, demand response etc.), R-DERs (wind turbines and PVs), and the distribution network equipment. Simulation studies were performed on this test platform. The results indicated that the closed loop MPC strategy had a much better overall performance (lower cost and higher wind utilization) under varying wind penetration levels and over different wind profiles for different days. The proposed control strategy was further extended by including demand response (DR) in the dispatch problem. Studies were performed to demonstrate that optimal coordination of DR with the other DERs can further reduce the fuel costs of the conventional generators and increase the wind utilization in the system. Further investigation is needed, however, to determine the real-time power and energy constraints for demand response.

In an ongoing collaboration with both the University of Florida and University of Illinois at Urbana-Champaign, the performance of the MPC based dispatch strategy was further improved. A parameterized Q-learning algorithm is devised to approximate the optimal terminal penalty function for MPC. It was shown that the combination of MPC and Q-learning approaches lead to a better solution in terms of computation, and adaptability to a changing environment. A proof-of-concept decentralized control strategy for C-DERs (demand response, distributed generators, and distributed storage) was also developed for contingency support. The objective is to arm and modify settings of the resources to adapt their response to current system/resource conditions and needs.

PN12017/2418

Decision Support for Future Power Grid Organizations

Gariann M. Gelston

This project examines human and organizational influencers on distributed decision making among power grid operators. After investigating causes of communication errors, we designed a prototype decision-support assessment tool as an analytical method to improve distributed decision performance of individual operators, with contributions from a variety of grid organizations.

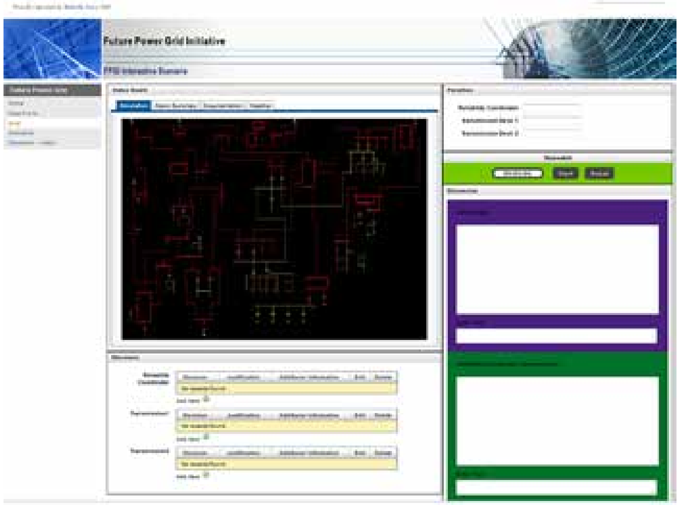
Rapid and effective response to unknown, undefined, or unplanned system events is a core challenge for the grid operator community. This project analyzes how inter-organizational communication and coordination among grid entities is currently practiced, and examines distributed decision making under uncertainty. To that end, we developed a prototype decision support assessment system to investigate rapid, adaptive decision making to target enhancements for improved grid reliability. While previous human factors research focused on improving individual operators' situation awareness and performance, we examined operational communication and coordination to address grid contingencies on an organizational level.

Our goals included developing a role-based communication framework to represent grid system decision makers and inter-organizational relationships; engaging the North American Reliability Corporation (NERC) and grid organizations to advise tool development; developing an analytical approach to understanding operator decision making; integrating with other projects by sharing industry contact and lessons learned; and developing publications to document technology development effort.

Important project findings from FY 2011 suggest that for unknown, undefined, and unplanned contingencies, automation cannot fully replace operators' decision making; the type, nature, and frequency of communication for distributed industry decision making is highly variable and complex, making a one-size-fits-all approach unlikely to represent this operational reality; and both systematic modeling and in-depth organizational studies are needed to enhance the empirical validity and generalizability of project outcomes. With these findings, the project team developed a prototype in FY 2012 for an interactive multi-organization decision-support assessment framework. The interface has the capacity to display images of a grid event rendered by a dispatcher training simulator and is designed to allow plug-and-play evaluation of a variety of potential decision support visualization technologies. The framework equips operator organizations with multiple communication options and records the information exchanged among decision makers across organizations. The recorded communication data can be analyzed to provide insight into how communication relates to grid contingency response effectiveness.

We presented our research at NERC meetings and conducted multiple site visits to major grid organizations. A critical feedback from industry experts highlighted a lack of existing economical training technologies and absence of a targeted tool to analyze operator communications. To address these issues, we will incorporate new features (such as voice chat) into the multi-organization decision-support and training framework in FY 2013 to improve operational capability. The team also received segments of real operational communication data from grid organizations that will be the basis of a systematic communication analysis scheduled for FY 2013. We will continue collecting and analyzing communication data from grid organizations and share research findings with industry partners.

Our project links across expertise in visual analysis, human factors, organization behavior, and emergency response to develop an organization-driven view of distributed decision support. This project will lead to an in-depth understanding of the key decisions, decision timescales, and challenges in organizational communication and coordination; help enable 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.



The multi-organization decision-support assessment framework, powered by CORE^{TM}, has an uncomplicated user interface to facilitate an interactive power grid distributed decision-making exercise.

PN11020/2342

Development of a Regional Energy and Infrastructure Systems Framework

Michael C.W. Kintner-Meyer

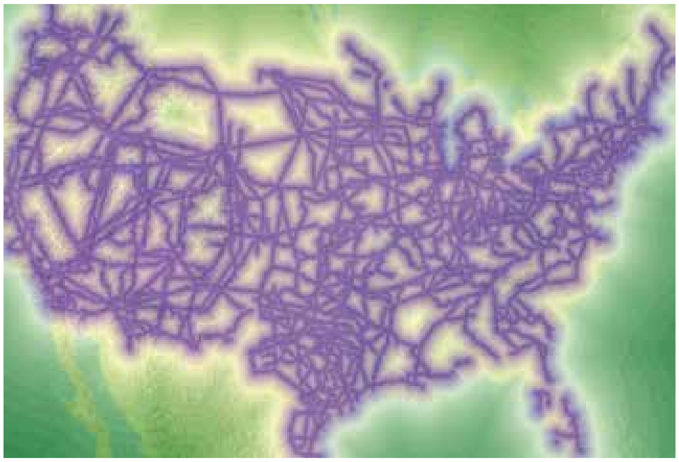
This project is developing a Regional Energy Infrastructure Framework (REIF) consisting of tools and models to analyze climate change impacts and associated mitigation and adaptation strategies for the energy infrastructure. REIF is a critical component of the larger integrated Regional Earth System Model (iRESM).

The iRESM research and development activity is developing and testing new systems modeling frameworks and tools that integrate climate with hydrology, land systems, socioeconomics, 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.



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

In FY 2012, our project accomplished the following with each model:

SITE model. We completed the consolidation of iRESM relevant GIS data into one consistent format that 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 enhanced and tested the open-source GIS analysis tools to perform large-scale queries to identify suitability of land given a set of complex criteria. Further, it computes distances functions from any location to existing energy infrastructure and natural resources, such as body of water or rivers.

PN10022/2264

We started and completed an evaluation of the SITE model based on 11 years (2000–2010) of power plant siting data. The evaluation refined the complex exclusion and power plant siting suitability criteria based on actual power plant siting documentations. The results of the evaluation are documented in a report and will be published as a peer-reviewed journal paper.

MELD model. We completed a full evaluation of the MELD model for the part of the 14-state Great-Lake pilot region. This included a parameter estimation that seeks the weights for 5 residential and 11 commercial building types at 6 different sizes, 7 vintages, and 3 different HVAC systems to match the combined load simulated by a building simulation program to the system load in that region. The outcome of the evaluation is a calibrated model of the building stock that matches both hourly electric loads as well as total electric energy consumption in a region. This model represents the building stock as well as the load behavior to with respect to weather.

EOM model. We initiated a new model development that represents the operations of power plant dispatch of power plants within a bulk-power transmission network. Previously, we used a utility-grade production cost model called PROMOD to perform this functionality for the iRESM effort. The new model development of the EOM is an open-source model. We compared the cost-optimal dispatch of the new EOM model with that of PROMOD and evaluated the differences. We also 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 suggest a high sensitivity of the electric grid with respect to hot and humid conditions over longer periods of time.

During FY 2013, we will work toward accomplishing the following tasks:

- evaluate and test coupling/interactions with other iRESM models
- integrate EOM with SITE and BEND/MELD, and complete testing.

Development of Rechargeable Li/air Batteries

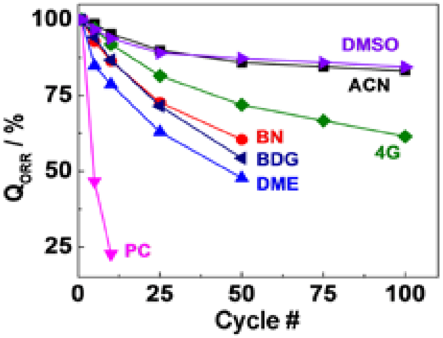
Jason Zhang

The main goal of this project is to investigate the rechargeability of lithium (Li)-air batteries and understand their fundamental mechanism.

Li-air or Li-oxygen (O_2) 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 Li ion batteries. Although several authors have reported significant rechargeability in Li-air batteries, there are still many questions about and uncertainties surrounding their stability. Advanced batteries with high energy/power density, good reliability, affordability, and environmental friendliness are critical energy storage devices worldwide for plug-in hybrid electrical vehicles (PHEVs) and pure electrical vehicles (EVs). While the current Li ion battery technology can satisfy the short-term need of EVs, higher energy density battery technologies are required for the long-range operation of the next generation of EV applications in which the rechargeable Li-air battery is one of the most promising future energy storage systems.

During FY 2012, we first studied the effects of six different types of aprotic organic solvents on the discharge performance and discharge products in Li-O_2 batteries. The aprotic solvents were selected from ethers or glymes, sulfoxides, phosphates, nitriles with long chains (which are stable with Li metal) and ionic liquids, and compared with carbonate solvents. Ketones, lactones, and carboxylate esters were not studied because all of them have –C(=O)– group in the molecular moiety as the carbonate solvents, which make the solvent molecules unstable against superoxide radical anion and its related products. Using these electrolytes, Li-O_2 batteries were assembled and discharged under similar conditions. The reaction products formed on the carbon-based air electrodes during the discharge process were systematically analyzed using various techniques, including x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), gas chromatography-mass spectrometry, and solid-state ^{13}C-magic angle spinning nuclear magnetic resonance (NMR) spectroscopy.

The results indicated that among the studied solvents, only glymes could lead to significant formation of Li_2O_2 (which is desired for reversible Li-O_2 or Li-air batteries) during the discharge process of the Li-O_2 batteries, although a small amount of Li_2O_2 was also generated from phosphate, nitrile, ionic liquid, and sulfoxide. However, Li_2CO_3 and LiF were also present in the discharged products of Li-O_2 batteries using all the six types of solvent systems studied, including the glymes. Less Li_2CO_3 and much higher discharge capacity were found in Li-O_2 batteries using butyl diglyme (BDG) as the electrolyte solvent. The effects of various solvents on the rechargeability of Li-O_2 batteries have been systematically investigated. The figure below compares the cycling stability of Li-O_2 reaction on glass carbon electrode in various solvents. Among the investigated solvents, dimethyl sulfoxide and acetonitrile solvent show the best cycling stability.



Comparison of the cycling stability of Li-O_2 reaction on glass carbon electrode in the electrolyte with various solvents.

We further investigated the effects of Li salts with different anions on the discharge performance and discharge products in Li-O_2 batteries. Seven Li salts were tested in Tetraglyme in the rechargeable Li-O_2 batteries. The discharge products were analyzed by XRD, XPS, and NMR spectroscopy. The electrolyte salts were found to have a drastic effect on the performance of Li-O_2 batteries. Significant decomposition of $LiBF_4$ and LiBOB to form LiF and Li borates respectively was confirmed by XRD and XPS. Li_2O_2 was identified as the major discharge product for the rest of the electrolyte salts. LiTf and LiTFSI were the best among the studied Li salts.

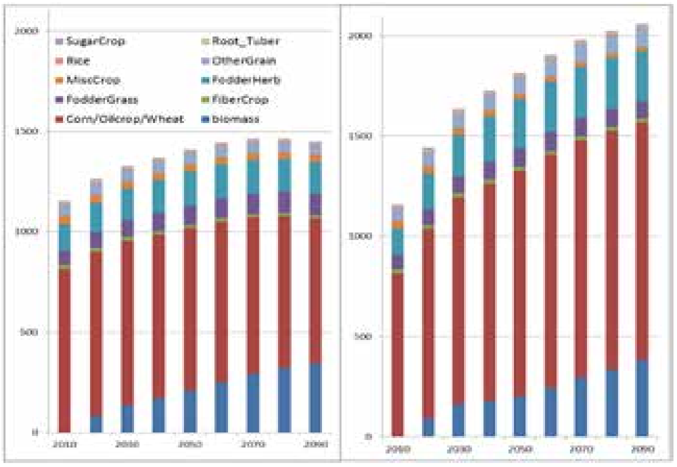
It is noted that all common organic solvent and Li salt are more or less unstable during the operation of Li-O_2 batteries. This instability may also be related to the catalytic effect of carbon based air electrolyte. Therefore, more efforts are required to develop new electrolyte systems (including solvent and salt) and new substrates that can work toward reversible and stable Li-O_2 batteries. The results of this project research in two journals, *Advanced Functional Materials* and the *Journal of Power Sources*.

Development of Regional Agriculture-Land Use Models

Allison M. Thomson

Our work developed an advanced capability for simulating climate impacts on agriculture and forestry to allow investigation of adaptation needs and mitigation potential of land management. With this information, decision makers can use this information to pose questions about food security and greenhouse gas mitigation from regional-scale agriculture of interest.

Climate change and food security are global issues that are increasingly linked through decision making that takes place across wide scales from on-farm management to international climate negotiations. While still supplying sufficient food to feed the global population, understanding how agricultural systems respond to climate change through mitigation or adaptation 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 also incapable 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.



Total crop production in the U.S. Midwest: no policy (left side bar chart) and with the Climate Mitigation Policy (right chart).

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 the Regional Global Change Assessment Model (RGCAM). The initial phase of our approach focuses on a pilot region of the U.S. Midwest. 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 U.S. Department of Agriculture (USDA) data and remote sensing products, to inform GCAM. This process will enable integrated assessment to account for crop yield, bioenergy production, soil carbon, greenhouse gas emissions, and economic costs of different agriculture management practices. With this information, GCAM can simulate the optimum mix of land management to achieve specific climate mitigation or adaptation targets.

In FY 2012, we completed model development required to initialize RGCAM with EPIC model results for the selected crops, management systems and subregions in the Midwest pilot area. The input data were assembled for the 2005 base year from a combination of USDA inventory information and EPIC model simulations. EPIC was parameterized to simulate major crops under traditional management as well as with residue removal for bioenergy and no tillage practices for soil carbon sequestration. In addition, dedicated bioenergy crops for cellulosic biofuels were also simulated. The resulting GCAM-USMidwest-AgLU model has been run for the 21st century under both reference case and global climate mitigation policy assumptions. In addition, a downscaling procedure was developed to allow the resulting subregional GCAM output to be re-mapped to the EPIC 56 m resolution crop systems.

The resulting findings indicate several important insights about the role of U.S. agriculture in global climate mitigation. Overall production in the region of interest increases, which reflects the high relative productivity of food and energy crops and the opportunity for crop residue removal for additional bioenergy resources.

This capability will be expanded to incorporate climate impacts on crop yields using the EPIC model driven by climate projections to inform future production in GCAM. The work will also be expanded to the U.S. Gulf Coast region under a newly funded project to explore climate adaptation opportunities in agriculture, in addition to the mitigation considered in this current work.

PN10029/2271

Forward Osmosis System for Integrated Desalination and Carbon Dioxide Separation

James R. Collett

We are transforming the economics of carbon capture and storage (CCS) by integrating new forward osmosis technologies for the desalination of brackish groundwater or seawater with CO_2 separation systems at fossil fuel power plants.

Recent studies indicate that the deployment of current commercial technologies for CO_2 CCS at coal combustion power plants will increase the cost of the electricity they produce by more than 80%, where DOE's targeted cost increase limit for such systems is 35%. Thus, both greenhouse gas emissions management and sustainable water use present core scientific and technological challenges. We propose to meet both of these challenges by developing an integrated approach for post-combustion CO_2 capture and water desalination using a forward osmosis system. We developed this novel approach to reduce the cost of CO_2 capture by integrating the process with the new system that can produce valuable fresh water as a byproduct of CO_2 capture. The successful demonstration of this approach could profoundly change the way CCS is viewed by the public, from a perception that it is a tax on energy consumption to an appreciation for it that can facilitate desalination technologies that provide drought-stricken communities with the water that they will need to grow into the future.

The objective this project was to obtain a preliminary assessment of potential cost savings and changes in energy requirements that would result from the integration of a forward osmosis (FO) water desalination system within a 550 MW supercritical coal power plant equipped with a solvent-based CO_2 capture system that removes 90% of the CO_2 from the plant's combustion flue gas. The analysis included technical and economic parameters to estimate the degree to which the cost of CO_2 capture could be mitigated if the plant were also capable of producing and selling high value fresh water made from brackish groundwater or seawater. This work addressed a core PNNL mission, transforming energy systems, by charting a path for the demonstration and deployment of a new clean energy technology.

In our envisioned approach, combustion flue gas is directed into a solvent spray tower, wherein the CO_2 in the flue gas is absorbed into a concentrated aqueous ammonia solution. This CO_2-rich solution is then routed into a bank of FO membrane modules to serve as a high-osmolarity draw solution for the separation of pure water from brackish groundwater or seawater. Within the membrane modules, the rich solvent is diluted five-fold, as pure water moves from the saline feedwater side of the membrane into the higher osmolarity draw solution. The diluted draw solution is then routed into an innovative distillation process that generates 1) a 90% pure CO_2 gas stream for compression and transport to an underground carbon storage site; 2) an ammonia vapor stream that is returned to the flue gas absorber; and 3) a stream of pure water from the distillation reboilers that may be used as makeup water at the plant or sold for municipal, agricultural, or industrial use. The key advantage of the integration of FO desalination unit operations within a solvent-based CO_2 capture system is that the high molarity aqueous ammonia can serve both as a sorbent for CO_2 from flue gas and as a volatile, high osmolarity solute in a draw solution for FO desalination, thereby reducing capital and energy costs of CO_2 capture and desalination.

Our findings indicate that a 550 MW coal-fired power plant equipped with our proposed technology could produce up to 26 tons of desalinated water per day from 2.5% TDS seawater for each ton of captured CO_2, thereby generating a fresh water output stream of 91 M gallons per day (MGD). Moreover, desalinating brackish groundwater with a much lower salinity (0.5% TDS) could generate 48 tons of fresh water per ton of CO_2, for yield of up to 167 MGD. The current total unit cost for desalinating brackish groundwater at a new, 100 MGD reverse osmosis plant in Texas was recently estimated to be $3.59/1000 gallons. At this price, a power plant equipped with our proposed technology could competitively sell its output of desalinated fresh water for a gross revenue stream of up to $220 M per year. This revenue could be used to offset the expense of CCS at the plant by up to 57%, thereby lowering the cost per ton of avoided CO_2 emissions from the current baseline of $75/ton down to $32/ton. We also estimated that the combined heat duty required for simultaneous FO desalination of seawater and ammonia-based CO_2 capture at the plant would be 736 MJ/sec, which is similar to our derived estimate of 684 MJ/sec for the same plant equipped with a conventional, amine-based CO_2 capture system instead.

Our initial assessment indicates that the integration of FO desalination within a CCS framework provides a promising strategy for achieving the DOE's goal of reducing the economic penalty imposed by current carbon capture technology. The integrated CCS/FO desalination approach merits further experimental development in the laboratory to lay the foundation for pilot-scale demonstration of the proposed technology at an actual power plant.

PN12034/2435

Future Power Grid Control Paradigm

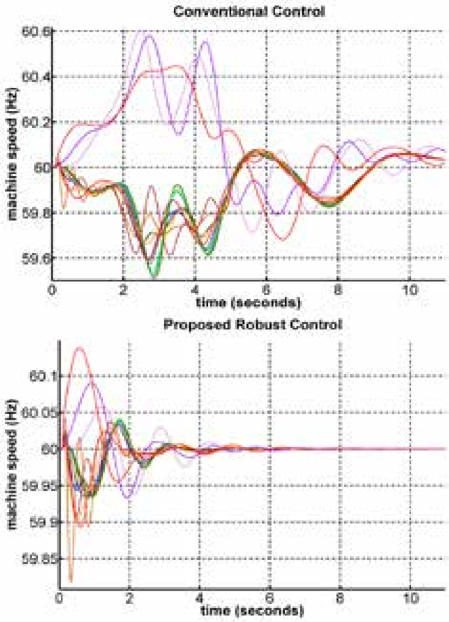
Karan Kalsi

This project proposes a novel control paradigm that enhances reliability and efficiency of the future power grid by exploiting the value of new monitoring and information technologies coupled with new business needs and policy changes. This will lead to creating a more flexible and reliable U.S. energy infrastructure.

With the premise that transmission system loading will continue to increase and the trend will be toward maximum utilization of transmission system close to thermal capacity, security and reliability will are crucial issues for the future power grid. The problem of power system security and reliability is evident considering past events such as the 2003 Northeast Blackout, which swept out a large geographical area in 9 seconds, affected 50 million people, and caused ~ $10 billion dollar losses. With the advent of the smart grid, the current power grid requires a new look at monitoring and operation capabilities and a new from-the-ground-up design of the control architecture.

Despite technological advancements, the monitoring and control capabilities of the power grid are still based on the conceptual design of the 1970s and 80s; i.e., current control strategies rely on offline planning studies and lack good real-time spatial and temporal coordination. While many ideas address specific control needs, this work reevaluates the power system control paradigm based on availability of new technologies and proposes applicable solutions that will lead to a resilient, self-healing future power grid. Specifically, we offer a conceptual control architecture that emphasizes real-time coordination of control schemes temporally and spatially to maximize operation margins or efficiency. This novel control paradigm minimizes impact and exploits the potential of smart grid technologies, leading to high penetration of clean, environmentally friendly renewable energy resources and non-conventional loads.

In FY 2012, we proposed a novel modeling framework that represents multi-machine power systems as large-scale interconnected systems. A subsystem is defined as a collection of substations (consisting of none, one, or more generator groups, transmission lines, and loads). Next, a distributed hierarchical controller design was proposed that facilitates frequency restoration and power balancing functions to be decoupled and implemented at different levels. At the local level, robust decentralized generator controllers are designed to improve transient stability and restore system frequency after faults and disturbances in the system. At the area level, automatic generation control is modified and coordinated with decentralized robust controllers to restore tie line power to their scheduled values. The efficacy of the proposed distributed hierarchical coordination control architecture is demonstrated by testing it on the IEEE 16-machine 68-bus test system and on the 17-machine simplified WECC system model. We demonstrated that proposed control achieves enhanced transient stability over the conventional control methodology under different types of contingencies and system disturbances.



Enhanced transient stability of proposed robust control over current controls.

Another goal for FY 2012 was to study the interactions of typical remedial action schemes (RAS) with the distributed hierarchical controller and to identify a path for optimal coordination of these two control actions. We demonstrated that the proposed robust control strategy can reduce the burden on the RAS, which in turn reduces the system stress due to tripping of generators. Finally, we proposed and tested a novel control framework to address the voltage stability issue, one of root causes of the 2003 blackout. The principle for this new scheme coordinated different voltage resources (e.g., flexible load consumption, generator reactive power, and capacitor switching) in an optimal, more efficient way using model predictive control.

In FY 2013, distributed dynamic state estimators will be designed for feedback in the distributed hierarchical robust controller designed in FY 2012 to drive the overall closed-loop system. Also, the work in FY 2013 seeks to coordinate the voltage control schemes with robust controller and remedial action schemes to provide multiple defense plans for the future power system. The robustness of the distributed hierarchical output feedback based coordinated control will be tested with a high penetration of wind and solar in the system. The proposed distributed hierarchical output feedback based coordinated control will be validated on the IEEE Standard test systems and on a simplified WECC model.

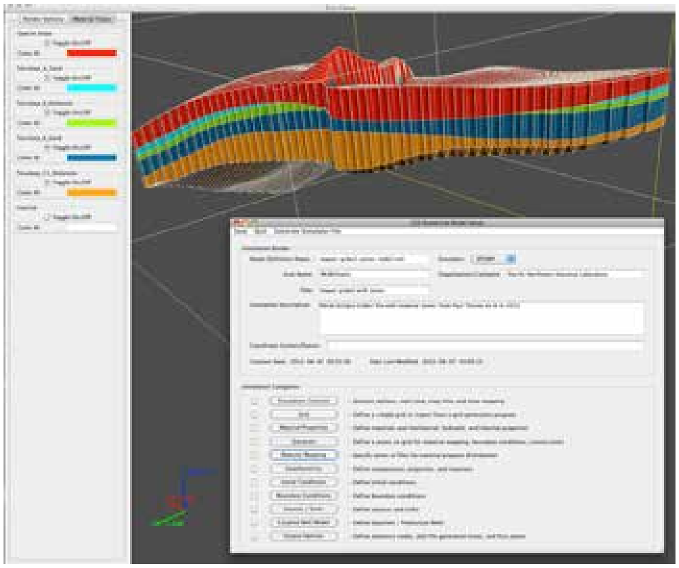
PN12035/2436

Geological Sequestration Software Suite: Numerical Model Development

Mark D. Williams

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.



Visualization of boundary fitted grid generated in Petrel/Eclipse (GRDECL file) with keywords for material distribution. Inset form shows top-level model definition categories of GS^3 numerical model development prototype.

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 provides 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 workflow was developed for exporting the numerical grid, assigning properties to the grid within Petrel or EarthVision, and importing the zonation back into the model definition process.

Progress during FY 2011 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 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.

Progress during FY 2012 included supporting additional features of the STOMP-CO_2 simulator, using boundary fitted grids generated by Petrel/Eclipse (GRDECL files), enhancements to the grid visualization, and accessing grid files stored on the Alfresco CMS. The additional STOMP-CO_2 supported features are the coupled well model and more options for solution controls, material properties, and output variables. The GRDECL files are used to define a grid in Petrel/Eclipse, along with using optional keywords for defining the spatial distribution of materials in the grid and spatial distributions of a specific property (e.g., permeability or porosity).

In collaboration with the GS^3 platform project, prototype development started in FY 2012 on a STOMP Input Advisor. This tool will help guide conceptual/numerical model development and collect data for building numerical models or for conversion from another simulator.

The functionality of the GS^3 numerical model development prototype tool was demonstrated by reproducing the benchmark problems published in the FY 2012 STOMP-CO_2 manual (except for the geochemical reaction network case which is not currently being supported by this GS^3 tool). An uncertainty quantification simulation software demonstration was developed across the GS^3 projects in FY 2012 that applied the numerical model definition tool for building the initial simulation base case. This base case was then used for selecting model parameters to vary and launching/monitoring/visualizing the simulations using tools developed by other GS^3 projects.

High-Capacity Reversible Metal Hydride Air Battery

Ewa C.E. Rönnebro

Envisioning a sustainable technology, this project aims at providing 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 (MHAB), a higher capacity, robust, long-life technology. This breakthrough in battery 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 MHAB that can be manufactured using low-cost, domestically available materials and processes. Our approach combines 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. For grid-scale applications, the cost and performance of existing high-capacity energy storage are limiting factors. By advancing the MHAB, we will obtain a higher capacity, robust, longer -life technology.

Within the research context, the commercial nickel metal hydride (NiMH) 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. Our approach is to replace the capacity-limiting nickel hydroxide cathode with a lightweight bi-functional air cathode. Because the cathode in a MHAB does not limit capacity, we can use high-capacity metal hydrides. To accomplish a battery with superior capacity, we focused on developing anode materials and efficiently screening through candidates. The key to success is developing the corrosion-resistant anode material, during which we considered two main approaches: the application of a protective coating on the metal hydride and tuning of the alloy with corrosion-resistant metals. The ultimate goal is to deliver a novel anode material with superior capacity and cycle life relative to the state-of-the-art.

When the project commenced in FY 2011, our main goals were to design and fabricate a screening capability to identify promising high-performing metal hydride candidates; to show proof-of-concept of a small-scale prototype of the MHAB; and to down-select advanced anode materials concepts. During FY 2012, our key accomplishments were having demonstrated improved performance of a coated metal hydride anode material obtaining 50 cycles and identifying some promising high-capacity metal hydride candidates with greater than 400mAh/g.

The main challenge to realize the MHAB technology is that the high-capacity metal hydride material corrodes in the water-based electrolyte. A specific focus in FY 2012 was, therefore, on anode materials development, as well as demonstrating the superior performance of advanced high-capacity metal hydride materials by using the two previously mentioned approaches. In FY 2011, we designed and manufactured an anode screening capability made up of nine electrochemical test cells to effectively screen for high-capacity metal hydride materials. These test cells are based on a metal hydride anode and nickel hydroxide cathode, similar to a NiMH battery. During FY 2012, high-capacity materials and new anode concepts were screened through with respect to their performance (i.e., capacity and cycle life), and promising candidates were down-selected. Based on a sol-gel synthesis route, we invented a layer-by-layer silica based coating approach that enabled longer cycle life of approximately 50 cycles and relatively higher capacity of our metal hydrides materials compared to uncoated materials.

Additionally, in collaboration with the University of Missouri-St. Louis, we explored new quasicrystal metal hydride anode materials, obtaining greater than 40 cycles with no capacity loss. In the future, we will combine our new coatings with the tuned metal hydride materials to obtain superior capacity of the metal hydride air battery to exceed 400 mAh/g.

PN11037/2359

Modeling of Distributed Energy Resources in the Smart Grid

Shuai Lu

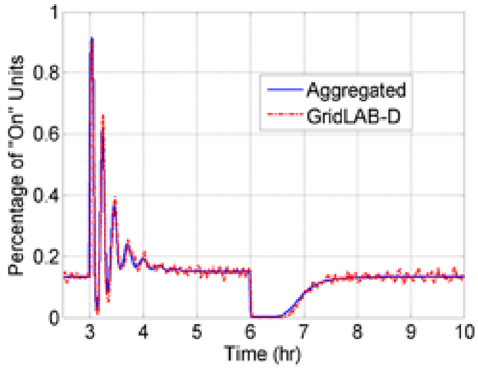
This project will develop aggregated models for distributed energy resources (DER) in the smart grid, particularly demand response.

To build a more reliable, efficient, 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.

This project is developing aggregated models that will represent the dynamic or steady-state characteristics of a large population of DERs in the design, planning, and operational studies of the smart grid. The work is very challenging in that it requires multi-disciplinary knowledge of various areas, including 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.

In FY 2012, this project made significant progress in the following activities: aggregated HVAC and electric water heater modeling, electric water heater field experiment for model validation, sensitivity study and uncertainty quantification on the parameters of the HVAC model, characterization of HVAC demand response performance, dynamic Bayesian network (DBN) model for HVAC load forecast, and multi-scale modeling of transmission systems with demand response.

DBN and state transition (ST) model were the two approaches initiated in FY 2011 to derive the aggregated models for thermostatically controlled loads (TCL), such as HVAC units and water heaters. In the first approach, DBN used training data obtained from a simulation of detailed models from GridLAB-D to obtain appropriate model structure and parameters. The DBN model is then adjusted using expert knowledge and test data. In real-world applications, the training data are expected to derive from historical data accumulated from operations (e.g., a load aggregation company operating a large amount of demand response devices). The trained DBN will help to forecast the availability of resources and estimate the distribution of device parameters. In the second approach, ST model aggregates the TCL devices being modeled into a few states of temperature. The transition of 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 models were compared with that from the detailed model (GridLAB-D) for accuracy.



Result of aggregated state transition model and detailed simulation (GridLAB-D) of 10,000 home models: A/C load response under sequential set point changes (T set = 75 -> 74 -> 75°F).

In FY 2012, we also performed a week of experiment on an electric water heater in a model home on the PNNL campus, in which data were collected to validate the individual water heater model (the basis of the aggregated model). Sensitivity studies and uncertainty quantification on HVAC model parameters were also performed to determine the uncertainty range of simulation results and identify important parameters for the construction of the model. To assist the design of demand response controllers, properties of HVAC response to control signals were characterized. Response speed and magnitude can be derived from the study results to determine suitable power grid services that can be provided by HVAC demand response. Also, the methodology for multi-time scale simulations was developed to study the transmission system steady-state and dynamic behavior with demand response in the same simulator.

For FY 2013, calibration techniques will be applied to aggregated HVAC and electric water heater models to obtain the correct set of parameter values for a population of devices. Methodology for developing aggregated demand response models will be integrated, which includes the DBN and ST models, uncertainty quantification, and model calibration.

PN11053/2375

Novel Carbon Capture Materials

David L. King

This project supports investigations of leading candidate materials (solids and liquids) for efficient, cost effective capture of CO_2 from post-combustion processes such as coal combustion in pulverized coal power plants, and pre-combustion such from coal-or biomass gasification.

The use of fossil fuels for power generation, especially with large coal-based plants, has the potential to adversely impact the world climate 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), and for this reason minimizing the cost of CO_2 recovery is a significant driver in technology selection. The overall goal of this project is to develop a portfolio of novel, cost-effective, material-based approaches for the capture of carbon dioxide, primarily from coal-based power plants where CO_2 is present in the flue gas. Within this, an additional goal is the development of analytical capabilities to generate measurements which can be supplied to an analysis framework, a so-called Technical Readiness Level (TRL) gate analysis. This analysis identifies technical requirements that must be met in order for a technology to advance to the next level (advancing ultimately toward commercialization). 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.

In FY 2012, we focused development efforts for CO_2 capture via ionic liquid-type solvents (COBOLs), electrochemically driven pH swing CO_2 capture, and metal organic framework materials modified to make their surfaces hydrophobic to increase the discrimination for CO_2 adsorption over water. The project produced a significant paper study aimed at identifying possible large cost saving through the co-removal of CO_2 and other gaseous impurities in a single unit operation. Finally, this project supported small paper studies and analyses aimed at determining if alternate methods of O_2/N_2 separations (besides cryogenic) could be identified, making oxycombustion of coal viable and developing numerous other opportunities. We were also provided support for initial work aimed at developing a CO_2 membrane for pre-combustion CO_2 capture.

Specifically for 2012, we continued support of two investigations from 2011 (CO_2-binding organic liquids [CO_2BOLs] and pH swing CO_2 capture in aqueous medium), and we initiated several short projects. Additional results are summarized below.

CO_2BOLs. Beginning in FY 2012, this project gained funding from the National Energy Technology Laboratory (NETL) for CO_2 capture from coal-based power plants (post combustion). Additional opportunities were seen for this type of material, specifically for application in removal of CO_2 and H_2S, either from natural gas sources or pre-combustion of coal or biomass. A primary difference is the latter applications are generally applied at elevated pressures and in a reducing environment, whereas post-combustion capture is at atmospheric pressure in an oxidizing environment.

Attention has focused on ethyldiethanolamine (EDEA). For CO_2, EDEA has been tested for CO_2 capture as an aqueous solution but has not been evaluated as a stand-alone solvent. It appears to act like a physical solvent in terms of the strong dependence of uptake on partial pressure. However, overall data are consistent with a combination of chemical and physical absorption. MDEA shows virtually no uptake toward methane or higher hydrocarbons, important for natural gas separations, and EDEA is highly active toward H_2S. Evidence for strong interaction is seen at up to 1 equivalent H_2S per EDA, while above that level there is evidence for some additional physical adsorption. It appears that there is potential application of this material in preferential absorption of H_2S over CO_2 (α factor of ~10), far better than the industrial standard Selexol.

Integrated Emissions. Implementing CO_2 capture onto the emissions control train of pulverized coal power plants adds significant capital and operating burdens onto the cost of electricity. This sub-project was charged to take a holistic look at all emissions control forms to determine whether technologies that could control multiple regulated emissions simultaneously could be more cost-effective. This involved efforts to generate and assess new control concepts that could improve the cost-performance of a baseline system consisting of the best available control technologies for NO_x, SO_x, and particulate control, plus a CO_2 solvent absorption/stripping system based on mono-ethanolamine (MEA). High-level conclusions from the study include:

1. Equipment and operating costs for CO_2 control dwarf costs to control other contaminants. The low-cost application will probably control CO_2 as cost effectively as possible as the primary driver.

Control of other emissions will be opportunistic to an efficient CO_2 system. Keeping individual controls for NO_x, SO_x, and particulate may remain the best option.

2. The energy demands of the baseline MEA process are so large that implementation will reduce the electrical output nearly 30%. The plant will have to be significantly expanded or de-rated. Implementation costs of CO_2 are effectively the process equipment for the capture system and capital and operating costs to expand the plant.
3. Solvent based CO_2 absorption and capture employ relatively standard equipment (i.e., towers with engineered internals), but size pushes the limits of equipment designs. New approaches to "mega-sized" equipment or process packages need to be developed to reduce costs.

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. For FY 2011, a preliminary analysis of the concept was carried out as applied to a large scale power plant. The feasibility of using an electrochemically generated pH gradient to capture CO_2 from a power plant was demonstrated. Through an engineering analysis, the process could compete favorably with the current MEA technology, provided that a reasonable cell over voltage could be attained. Contributions to the overpotential included the IR drop in solution, flooding of gas diffusion electrodes, and kinetics of H_2 oxidation in neutral solution. Ultimately, the latter proved to be a limiting factor, but electrode flooding may still occur. Preliminary studies suggest that new catalyst materials may require development to overcome this problem. Most work in this area reported in the literature focused on either acidic or basic (but not on near neutral) solutions. We conclude that future work should focus on the mechanism of oxidation in neutral solutions, with careful examination of the catalyst type.

Development of Hydrophobic Molecular Organic Framework (MOF) Solid Adsorbents. MOFs are high surface area porous materials that combine organic and inorganic components in a variety of ways to generate multiple structures. For some time, MOFs have been of interest for CO_2 capture because of their high surface area and porosity; however, they absorb water competitively, which decreases their value in CO_2 capture for post-combustion. Moreover, some MOF materials are unstable in a steam/water environment. A novel approach suggested a method to modify MOFs toward increasing the moisture stability and minimizing water sorption without compromising CO_2 sorption capacity. Specifically, this approach incorporates hydrophobic moieties on the external surface of the MOFs via physical adsorption, with the aim of increasing surface hydrophobicity in the porous materials without the need of introducing bulky functionalities inside the pore. Support for this work began late in FY 2012. Preliminary work with MgDOBDC and the surfactant Pluronic P123 indicate that a reduction of H_2O adsorption relative CO_2 adsorption is promising.

Oxygen-Nitrogen Separation Using Perfluorinated Solvents. Two short studies examined new ideas for oxygen-nitrogen separation. The specific target would apply this separation to coal combustion (oxy-combustion), in which case the primary combustion products CO_2 and H_2O would not be diluted by N_2 gas introduced from air.

The first project examined using a perfluorocarbon such as perfluorodecalin as a solvent to extract O_2 from air. Such materials have been applied in artificial blood due to their capacity for O_2. However, using thermodynamic data, based on a surprisingly low preference of the fluorocarbon solvents for oxygen over nitrogen and the preferential solubility of CO_2 over oxygen, the concept as proposed would suffer both from ingress of nitrogen to the combustion loop through the solvent and from loss of CO_2 through the solvent to the atmosphere. Based on data, the fluorinated solvents would not be suitable, and a solvent with suitable properties is not known to exist. It was decided that no further investigation was warranted.

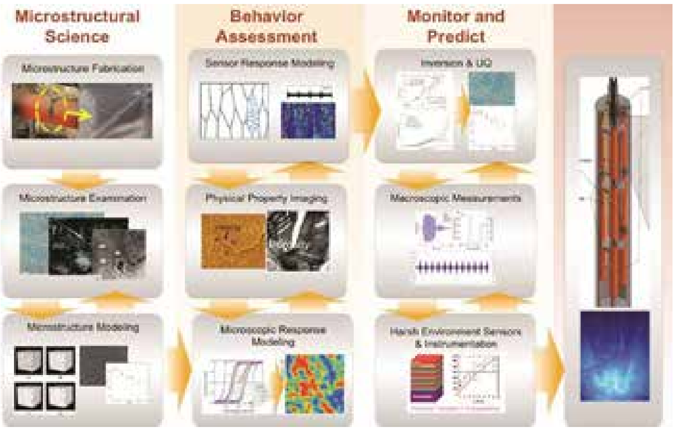
The second project explored the use of magnetic fields to separate O_2 from air, because O_2 is paramagnetic and N_2 is not. Calculations were made assuming linear field gradients. The derived equation shows that the density difference is enhanced by larger gradients, wider containers, lower temperatures, and higher fields. These results can be applied to "real world systems" to determine feasibility.

CO_2 Membrane Development. This project investigates the feasibility of developing a CO_2 membrane at warm temperatures (300–500°C) for its removal from syngas at elevated pressure. The specific composition is a $Na_2Mg(CO_3)_2$ double salt that shows reproducible uptake and release of CO_2 at around 400°C and partial pressures above 4 bar using a pressure swing operation. The physical properties of the materials are such that it has proven difficult to convert to a free-standing membrane. The conclusion of this work is that the double salt is best admixed with a high temperature polymer that can seal the cracks and fissures developed by the solid absorber. The seed funds for this project resulted in the acceptance of a separate project for FY 2013.

Novel In-Situ Monitoring Framework for Environmental Degradation of Reactor Structural and Fuel Materials

Robert O. Montgomery

We are advancing S&T to support real-time monitoring (RTM) of early degradation in structural and fuel materials used in nuclear power production. The development of such a capability represents a timely solution to the mounting issues that operators face with materials degradation.



Science-based framework for RTM of material degradation.

The focus of this effort is to move beyond the current approach of in-service inspection by periodic nondestructive examination of structural materials and toward using RTM of material degradation *in situ*. By detecting the early stages of material degradation mechanisms, better insights are gained about the material state that can be used to mitigate progression of the degradation or understand the margin to component failure. A critical step in achieving this objective is a science-based approach that relates changes in the underlying microstructural characteristics to detectable variations in the response of the material when external interrogating fields are applied to probe material structure.

This project consisted of three main technical thrust areas:

Microstructural science. We worked to understand the onset and progression of prototypical degradation mechanisms in materials under the influence of temperature, neutron irradiation, chemical attack, and other stressors.

Behavior assessment. We evaluated the degradation evolution mechanisms and the resulting changes in physical properties of the material (acoustic, magnetic, electrical) by meso-scale models and experiments to gauge sensitivity of measurement methods at early stages of damage.

Monitoring and predictive capabilities. We assessed environmentally hardened sensors to monitor materials behavior under harsh conditions and evaluated inverse analysis methods that attempt to quantify the level of damage at the microstructural level.

During FY 2012, the conceptual design for the science-based approach to *in situ* RTM of material degradation was performed, with the focus on reactor structural materials. The framework that arose from conceptual design studies includes: 1) use of advanced material characterization methods to understand initial material state conditions (grain size and orientation, texture, dislocation defect density, and residual stress conditions); 2) development of microscopic physical property imaging techniques that can detect the impact of lower-length scale microstructure changes on key material properties; 3) construction of meso-scale modeling methodologies to simulate the impact of microstructural changes on physical properties (coercivity, elastic constants, and electrical conductivity) and that can simulate sensor response to heterogeneous electromagnetic and acoustic properties; 4) development of advanced sensor materials and instruments for use in harsh environments; and 5) use of signal inversion and uncertainty quantification methods for damage state reconstruction.

Assessments were performed to evaluate the potential to use scanning probe microscopy methods (e.g., atom force acoustic microscopy, magnetic force microscopy, and piezoresponse force microscopy) to characterize the impact of microstructure features on physical properties. Recent experimental work has shown that changes in material magnetic or acoustic behavior can be from microstructural changes. The assessment identified several technology gaps for these methods, mainly the ability to sample large enough volumes to find rare features such as defects and crack precursors (impacts the fieldability of the RTM technique), the ability to generate models of microstructures with heterogeneous electromagnetic and acoustic properties (impacts the development of the RTM technique), and the ability to generate sensor models which statistically predict detection of damage for heterogeneous materials (impacts interpretation of the measurement).

PN12057/2458

Quantify the “State of Health” of Nuclear Structure/Materials with an Inverse Resonance Inspection Algorithm

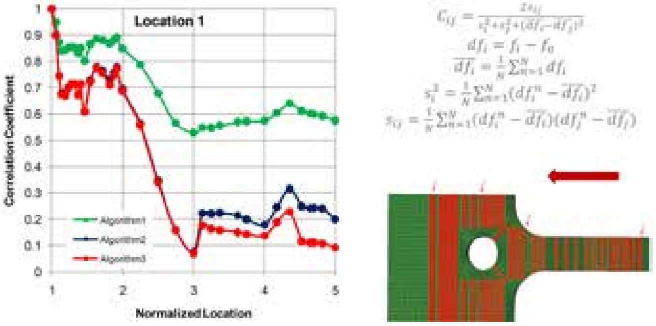
Canhai (Kevin) Lai

> ***Our research builds 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 the nation’s clean energy portfolio for environmental friendly sustainable growth. Currently, existing U.S. nuclear reactors account for at least 70 percent of low greenhouse gas-emitting domestic electricity production. Though the existing U.S. nuclear fleet has a remarkable safety and performance record, many 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 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 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 by developing an integrated experimental/modeling approach using inverse resonant ultrasound spectroscopy or resonance inspection (RI). Widely used in production, current RI technologies lack the specific means to identify the location and size of flaws. This project involves developing inverse algorithms, simulating finite elements, sample preparation, and experimental RI data collection. More accurate correlation algorithms will be developed to improve inverse resonance inspection to pinpoint structural flaws and build a prototype inverse RI algorithm software suite.

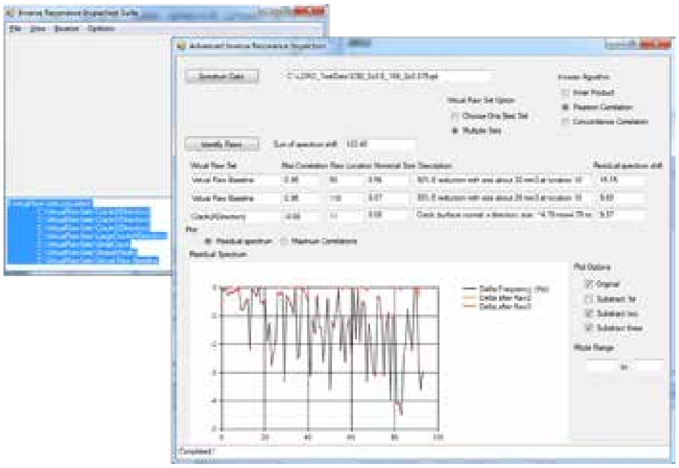
We achieved several important technical milestones in this 2-year project. In FY 2011, we developed a computationally efficient method based on linear perturbation theory to predict resonance frequency shift of a flawed part based on the finite element analyses of a perfect part. The results were summarized in a paper accepted 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 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.



Accuracy comparison of three inversion algorithms

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 were summarized in another manuscript (in press) for the *ASME Journal of Vibration and Acoustics*.

In FY 2012, we met our new reprioritized goals with a reduced project budget. We further improved the inverse resonance inspection algorithm and turned the prototype software suite developed in FY 2011 into a mature, advanced Inverse-Resonance Inspection Suite (I-RIS) for which we designed the sensitivity matrix and computational algorithm utilizing the database. The matrix consists



Inverse resonance inspection suite (I-RIS)

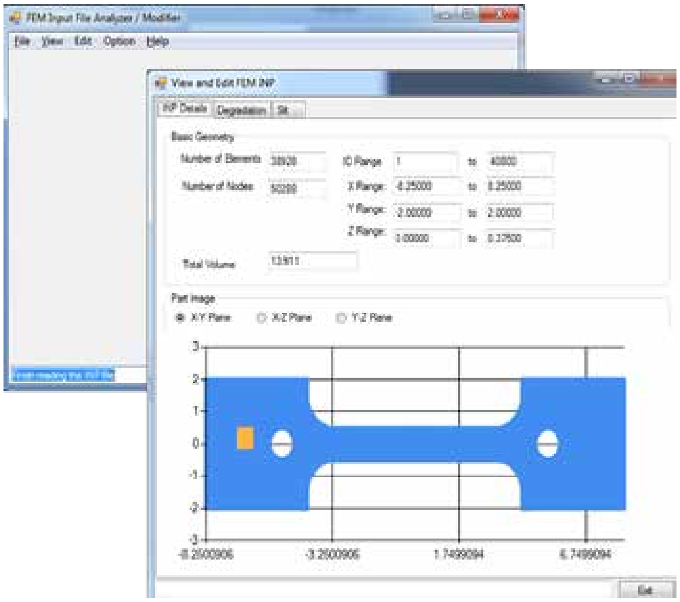
of several virtual flaw databases for various flaw types (degradations, voids, and cracks) at various locations and at various sizes, with sensitivity analysis also performed. As the I-RIS can import large numbers of virtual flaw databases, the iterative computational algorithm implemented can seek a combination of the highest correlation coefficient at each iteration step and the smallest residual frequency shifts in the end of iteration steps using all (or a specific) imported virtual flaw database. To find flaws in an unknown flawed part, users can manually choose which flaw database for the simulation or allow the algorithm automatically to find the best fit in each iteration step. The figure shows a snapshot of the software suite. Numerous simulations were run, which proved that I-RIS technology works for identifying the first three flaws with different types, sizes, and shapes at different locations.

A specific FY 2012 goal was to create many virtual flaw databases, each containing FEM simulation results for many flaws of the same category (i.e., degradation of the same size and same severity) but at different locations. This simulation task required an efficient way to introduce flaws virtually into the original part or inserting necessary changes in the FEM input file. To perform the task efficiently, a software suite named "FEM Model Analyzer/ Modifier" has been developed for this purpose (refer to FEM figure snapshot). The software reads an ABAQUS input file and allows a user to insert various flaws (voids, degradation, and cracks) with user-defined geometry and degradation factors.

With the help of I-RIS, numerous numerical simulations have been run to test the algorithm. Three different types of structural flaws (cracks, voids, and local stiffness degradation) and their various combinations were considered, from which flaw severity (size and degree of degradation) can be different from that of the virtual flaw databases. Numerical results showed that the proposed inverse RI algorithm can provide reasonably reliable and accurate predictions on both flaw location and severity. Because such flaw identification helps narrow potential damaged regions for physically direct visual inspection or other methods, this technique is expected to be particularly useful in quantitatively monitoring the structural health of active in-service engineering systems.

In this project, a maximum correlation-based iterative inverse algorithm for resonance inspection technology has been presented to identify the location and severity of structural flaws quantitatively when the frequency spectrum of an anomaly part with unknown flaws is available. The effectiveness of this methodology is evaluated by numerical studies on a stainless steel dog-bone sample with various types of virtual flaws (modulus degradation, internal voids, and cracks) using simulated virtual flaw databases. It is demonstrated that the proposed methodology can identify up to three unknown flaws with reasonable accuracy, even when a variety of flaws coexist. It shows that the prediction deviates when more and larger flaws get involved and when internal voids are mingled into the mixed flaws. The predicted damage weight was found to be proportional to the product of modulus loss and flaw size for modulus-degradation, while linearly dependent on flaw size for internal voids. These findings are believed to be helpful in establishing the quantitative estimation of the actual state of health of the engineering structures.

It should be noted that prediction accuracy of the current algorithm demonstrated on virtual cases hinges on the accuracy of frequency shifts between good and anomaly parts. In turn, this situation requires correct representation of the material properties/geometries of the undamaged structure in the numerical models and no subsequent frequency mode switches to be induced by small virtual flaws. The summation of the simulation work using I-RIS was submitted to the *ASME Journal of Vibration and Acoustics*.



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Y Range -2.00000 to 2.00000
Z Range 0.00000 to 0.37500
Total Volume 13.911
● X-Y Plane ○ X-Z Plane ○ Y-Z Plane

FEM input file analyzer/modifier

Validation through experimental data is crucial for I-RIS technology to be applicable to industry. For experimental tasks in FY 2011, we fabricated 30 structural parts and completed RI tests on them. The goal was to establish consistency between FEM predictions and experimental RI measurements for perfect and flawed populations. However, from challenges and factors such as RUS measurement accuracy, possible material property imperfections (heat treated vs. non heat treated), and geometry non-consistencies, the spectrum result comparison between FEM simulation results and experiment measurements was not as consistent as expected. With the reduced budget in FY 2012, work on the experimental side has shifted to future strategic planning. Specifically, we submitted two proposals, identified technology gaps, and attempted to establish collaboration with Vibrant Corporation, the industry leader for precise RUS instruments and measurements. Although the collaboration was not funded, our efforts provided a solid path toward bringing I-RIS from technology readiness level 3 (TRL3) to TRL5.

Accurate numerical representation of flaws in real life is another crucial issue to this inverse RI approach. For example and as elaborated in the previous section, actual cracks usually introduce stiffness reduction around the crack wake, and model the virtual cracks accurately requires additional characterization of the size of the flaw-affected region and severity of the degradation. In the end, because the algorithm developed is a general approach, more complicated flaw cases or complex flaw combinations can also be considered by establishing additional virtual flaw databases accordingly.

Restructuring FEDS for Continued Growth and Expanding Markets: GUI Update

James A. Dirks

This project adds capabilities to the energy management tool – the Facility Energy Decision System (FEDS) software – which is focused on modeling building system performance and determining the optimal retrofits for existing buildings.

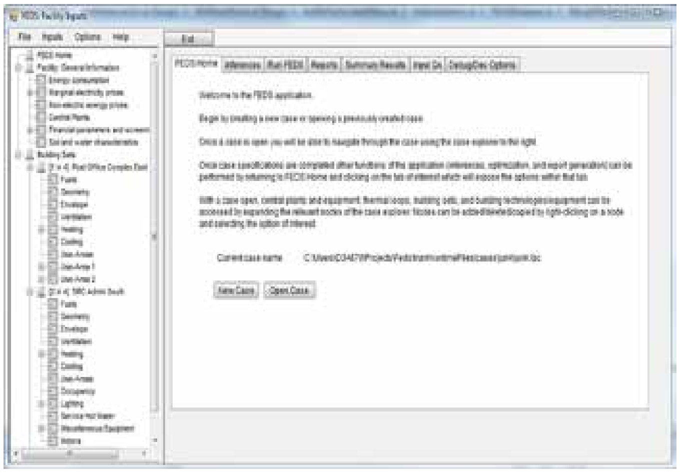
From advances in building codes, technology development, and design practices, it is assumed that energy use intensity of new buildings will be about half that of the average existing building. Further projections indicate that by 2030, buildings will consume 77% of available electricity; thus, one could surmise that existing buildings (those in place now) will consume more than two-thirds of the nation's electricity. To address energy security, grid security/stability, and carbon emission issues, then, one must look at the existing building stock. To combat these challenges, FEDS began as a modest investment in 1990 with the goal of introducing a tool for building energy efficiency investment opportunities. As affordable energy, energy security, and emissions reductions grow, significant interest in the analysis capabilities of FEDS has increased in kind. During the FEDS development years, desktop computing technology has also advanced significantly, mandating new features and capabilities that surpass the capabilities that the current code development platform can provide. For FEDS to continue as the analysis tool-of-choice, it needs to adopt the next generation of functionality and features.

The project objective was to introduce a new FEDS user interface as the first stage of investment in migrating FEDS to the next generation for implementing advanced functionality and analysis capabilities. The result of this effort will be a significantly more robust FEDS model and the ability to identify energy, cost, and emissions saving retrofits. The completed product will also provide modeling capabilities to identify cost-effective retrofits to existing buildings.

To meet project objectives, a new FEDS user interface was developed as a modern graphical user interface written under the Microsoft .NET code development platform. The approach focused on two main areas: converting the existing VB6 code to VB.net, and updating and increasing functionality to enhance the user experience, ease of use, memory allocation, and integration of graphical output. The first piece ported existing capabilities, including screens, input checking, and verification, to the new platform. Included in this process was an evaluation of capabilities in the new platform to maximize a more modern functionality. The second task added software enhancements, which included a "case explorer" tool for navigating between project input screens, a functional FEDS input screen resizing, an enhanced user guidance via tool and input tips, more comprehensive quality assurance features, a detailed input without first requiring minimum set input, and a new project "inference process" interface.

This project effort also included reorganizing how and where non-user interface activities were implemented. More specifically, any functionality that could be effectively used by future web applications or application programming interface technologies was removed from the user interface screens and into a newly added middle-tier code layer. This migration of code functionality to a "middle tier" has already been established by tools that require specific FEDS analysis capability but without the level of detail that the FEDS user interface demands.

All project goals were accomplished. The new user interface will allow moving forward more readily with new capabilities and enhancements.



Screenshot of the new "inference process" FEDS interface

Stabilized Li Metal Anode for Li Batteries

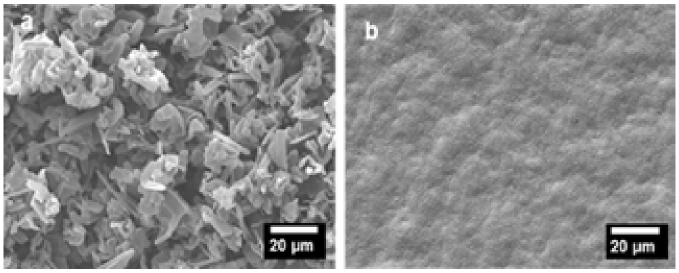
Jason Zhang

Rechargeable lithium metal batteries are considered "the holy grail" of energy storage systems. Unfortunately, uncontrollable dendritic lithium growth inherent in these batteries (upon repeated charge/discharge) has prevented their practical application over the past 40 years. A novel approach has been developed in this work to solve this problem.

Lithium metal has an extremely high specific capacity (3820 mAh/g) and low potential (–3.04 V vs. standard hydrogen electrode), which make it an ideal anode for high energy lithium batteries. However, dendrite growth and Li/electrolyte side reactions are the two main barriers that prevent its practical applications. After 40 years of limited work in this field, the urgent need to double the energy density of batteries used for electric vehicles and for development in nanomaterials drive a renewed effort around the world to improve the stability of the lithium anode.

In FY 2011, we performed a fundamental analysis of the lithium dendrite nucleation and growth processes using an approximate quantum mechanics method and systematically investigated the effects of various electrolyte solvents on lithium dendrite growth at the surface of the copper substrate during the electrochemical deposition process. We also developed special membranes to minimize lithium dendrite growth and found that nearly no dendrite formed at the surface when treated with hydrothermal crystallization; therefore, a zeolite membrane was determined to be a good protection layer to suppress dendrite formation.

In FY2012, we studied the effects of lithium salts with different anions in a cyclic carbonate solvent on morphologies and cycling efficiencies of lithium deposition films. We found that the salts of $LiPF_6$, $LiAsF_6$, LiTFSI, LiBOB, LiDFOB, and LiI could form a compact film to cover the copper substrate, but the deposited lithium films from electrolytes with $LiBF_4$, $LiCF_3SO_3$, and $LiClO_4$ were not good. The LiBOB salt resulted in wire-like lithium deposition morphology, which is quite different from other lithium salts. The salts of $LiPF_6$, $LiClO_4$, and LiTFSI also showed higher cycling efficiency and better cycling stability than other lithium salts. Therefore, LiPF6 was chosen as the standard salt for further studies.



SEM images of Li metal film grown on Cu substrates without additive (left) and with additive (right).

When testing the effects of electrolyte additives on the morphologies of lithium deposition films, we identified several salt additives that led to significant improvements on the smoothness of lithium metal films deposited in a copper substrate. For instance, when $CsPF_6$ was added to the electrolyte of 1 mole/liter (M) LiPF6 in propylene carbonate (PC), the dendritic morphology of deposited lithium film was changed to dendrite-free morphology at 0.01 M $CsPF_6$ addition. At 0.05 M concentration of $CsPF_6$ in this electrolyte, the lithium deposition film had a metallic mirror-like shining, suggesting the smoothness of the lithium film. This Cs-additive could effectively smooth the already formed lithium dendritic morphology in the continuous deposition. The *in situ* optical microscopic observation of lithium deposition in electrolytes with and without the $CsPF_6$ additive demonstrated lithium smooth growth in the Cs+-containing electrolyte but dendritic growth in the control electrolyte. In addition, the Cs-additive could improve the cycling efficiency and long-term cycling stability of lithium electrode for more than 400 cycles.

Based on our results, we proposed a novel self-healing electrostatic shield (SHES) mechanism to explain the effective prevention of lithium dendrite growth during lithium deposition and long-term charge/discharge cycles. It is under the assumption that an additive cation has an effective reduction potential lower than lithium cation achievable by the indication of the Nernst equation. During the deposition, lithium and additive cations are attracted to the existing lithium tip, but the additive cations are not reduced. This forms a positively charged electrostatic shield around the lithium tip that repels other positively charged cations so that more will be preferentially deposited in the adjacent region of the existing tip. This process continues until all substrate valleys are filled with deposited lithium, indicating the repeated self-healing process. Computational simulations on lithium deposition in $LiPF_6$-PC electrolytes with and without the $CsPF_6$ additive are consistent with the proposed SHES mechanism. SHES additives will not be consumed during operation so they can be used for long-term cycling. These promising results indicate that lithium metal can be used as the anode in rechargeable lithium metal batteries to achieve high energy density lithium batteries for electric vehicle applications.

PN11072/2394

Stable and High Voltage Electrolytes for Lithium Ion Batteries

Wu Xu

The commercialization of electric vehicles (EVs) demands advanced energy storage systems to have higher safety, lower cost, higher energy density, and longer cycle/calendar life than the state-of-the-art (SOA) lithium (Li) ion batteries. The development of new electrolytes with high thermal, high-voltage stability will significantly increase the lifetime and energy density of Li ion batteries, leading to more reliable products.

Advances in SOA Li ion batteries are critical to ensure high and safe energy storage devices for EV and grid applications. The SOA non-aqueous electrolytes based on lithium hexafluorophosphate ($LiPF_6$) and organic carbonate solvents contribute significantly to the safety problems and reduced lifetime of the batteries, especially the lithium salt $LiPF_6$ due to its thermal instability and moisture sensitivity. The formed byproducts are strong acid and Lewis acids that cause serious problems to the batteries, such as corrosion of electrode-surface-protection-films, dissolution of cathode active materials, and degradation of electrolyte solvents. Therefore, there is an urgent need to develop thermally and electrochemically stable electrolytes that are able to improve the safety, cycle, and calendar life of Li ion batteries for large-scale transportation applications.

The goal of this project is to develop non-aqueous electrolytes with thermal and high voltage stabilities by using more stable salts: lithium bis(trifluoromethylsulfonyl)-imide (LiTFSI) and lithium tetrafluoroborate ($LiBF_4$). The problems with LiTFSI (corrosion to Al, the cathode substrate) and $LiBF_4$ (poor capability of forming good solid electrolyte interphase films on graphite anodes) are addressed by adding appropriate additives.

As for the effort of protecting the Al substrate from corrosion by the TFSI anion, the cyclic voltammetry (CV) method was first used to test the current responses of the Al electrode with the change of scanning voltage in LiTFSI-based electrolytes with twelve different additives. It was found that two lithium salts, LiDFOB (difluorooxalatoborate) and LiBOB (bisoxalatoborate), with 2 wt.% in the electrolytes could protect Al from corrosion after the first scan. When the salt additive content increased to 3% and more, the protection could be occurred at the first anodic scan. The protection is due to the formation of dense inorganic and organic films on Al surface from the decomposition of these lithium salts.

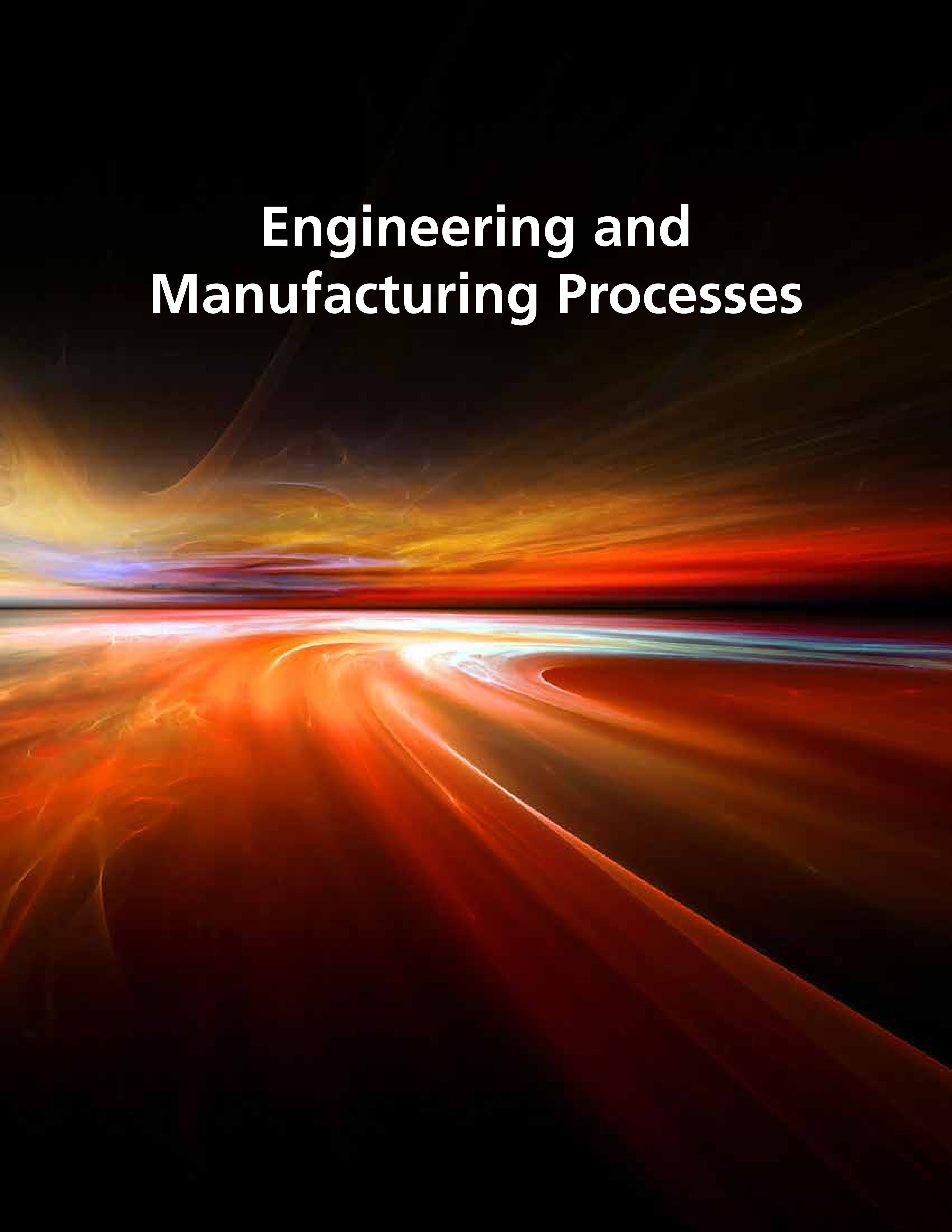
The effect of LiBOB as additive in LiTFSI-based electrolyte on the rate capability and long-term cycling stability of Li|$LiFePO_4$ batteries was evaluated in CR2032 coin cells. The electrochemical characterizations reveal that batteries with LiTFSI electrolytes have much higher capacities at high current rates than the ones with the $LiPF_6$ electrolyte, meaning LiTFSI electrolytes have better rate capability than $LiPF_6$ electrolyte, although the latter has higher conductivity. The addition of 3% LiBOB in the LiTFSI electrolyte leads to even higher rate performance. In addition, the two LiTFSI electrolytes (with and without the LiBOB additive) both show similar long-term cycling stability similar to the $LiPF_6$ electrolyte.

In the effort of replacing $LiPF_6$ with $LiBF_4$, 10 additives at 2 wt.% concentration in $LiBF_4$ electrolytes were tested in Li|$LiFePO_4$ and Li|Graphite cells, along with the comparative test of the $LiPF_6$ control electrolyte. In the Li|$LiFePO_4$ cells, nearly all of the $LiBF_4$-based electrolytes (with different additives) have a greatly enhanced rate capability over the $LiPF_6$ electrolyte especially at high rates, although the latter electrolyte has a much higher ionic conductivity. The $LiBF_4$ electrolytes also show higher discharge capacity and better capacity retention than the $LiPF_6$ electrolyte. Among the studied additives, LiBOB, LiDFOB, and vinylene carbonate are the best in both rate capability and long-term cycling stability. On the other hand, in the Li|Graphite cells, all studied additives can improve the rate capability of $LiBF_4$-based electrolytes over the $LiPF_6$ control electrolyte. These additives can also enhance the long-term cycling stability of the $LiBF_4$ electrolyte, but their stability is still not as good as the $LiPF_6$ based electrolyte, likely due to the eventual consumption of additives (only 2%) in the electrolytes. The optimal additive content needs to be further investigated.

It has been demonstrated from the above results that the thermally and electrochemically stable electrolytes based on LiTFSI and $LiBF_4$ are able to replace the unstable $LiPF_6$ with the appropriate additives at certain amounts for the use in $LiFePO_4$ battery system. In FY 2013, we will investigate these thermally stable electrolytes for their application on higher voltage, higher capacity cathode materials such as $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (charged to 4.1 V), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O2$ (4.4 V), Li-rich composite cathode (4.6 V), and $LiNi_{0.5}Mn_{1.5}O_4$ (4.9 V). More additives and additive concentrations will also be evaluated and optimized. Feasible electrolyte formulations based on LiTFSI and $LiBF_4$ will be developed to improve safety, cycle, and calendar life of Li ion batteries for EV applications.

PN12072/2473

Engineering and Manufacturing Processes



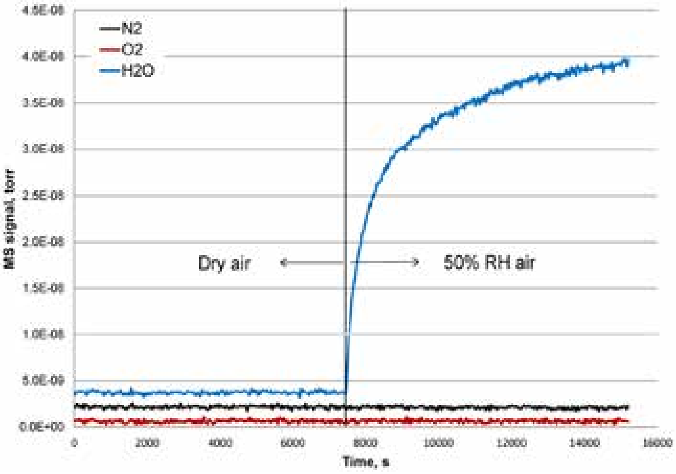
Development of Functional Membranes for Improved Selectivity

David W. Gotthold

We are developing new methods for making separation membranes to enable higher selectivity, improved transport, and extended lifetimes. The initial focus is on improved dehumidification membranes for application to metal-air batteries, building climate control, carbon capture, and natural gas processing.

To date, most membrane work has focused on specific material systems, polymers, metals, or ceramics. Hybrid system work has been primarily about the use of structural support as opposed to combining functional materials. The objective of this project is to achieve higher performance by combining different materials into a single membrane structure and developing processes necessary for scaling to manufacturing. To achieve this goal, we focused on two different approaches to improved selectivity membranes. The first was to improve the selectivity of standard membranes using applied electric fields and integrated porous thin film electrodes on standard polymer membranes to affect the relative transport of polar and non-polar molecules. The second approach was to evaluate the possibilities of a newly discovered graphene oxide (GO)-based membrane that demonstrated remarkable water vapor selectivity. Specific procedures and membranes used are highlighted below.

Capabilities. To test the membranes, a new evaluation system was assembled that enabled a range of gasses with varying water content to a test cell and permeate extraction using either a vacuum or carrier gas to a mass spectrometer for analysis.



GO membrane with selectivity for H_2O over N_2 and O_2 above measurement limit ($>10^4$).

Bias membrane. For this work, the focus was on determining the relative change in water transport with the application of electrical bias. The tested film was a commercial DuPont Teflon® PFA 125 µm thick membrane already under investigation for water permeation. Both sides were coated with sputtered Al (0.5 µm thick) after a 5-minute exposure to O_2/Ar plasma required for proper adhesion. The Al was then patterned using a pulsed excimer laser to produce a grid of 5 µm diameter holes on 20 µm centers. The film was tested using 50% RH zero air with biases up to 500 V; however, no changes in permeation were observed.

Graphene oxide membrane. This work was based on published results that showed GO has significant potential as a highly selective membrane for water vapor with selectivities $>10^{10}$. GO was prepared following the Tour group's published improvement over the commonly used Hummer method. Improved graphene oxide (IGO) is produced from graphite flake through oxidation with potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), and ortho-phosphoric acid (o-H_3PO_4). The IGO is recovered through multiple rinsing steps with distilled water and ethanol and re-suspended in fresh water and lyophilized to enable it to be re-dispersed.

GO membranes were prepared by filtration and consisted of several µm thick multilayer stacks of IGO molecules. Dry IGO was suspended at a 10 mg IGO/80 ml water using bath sonication followed by stirring. Aqueous suspensions of IGO were drawn through 47 mm diameter membranes using a filtration apparatus with mild vacuum. Free-standing IGO membranes were prepared on anodized alumina membranes with 0.02 to 0.2 µm pore size. The air-dried IGO membrane was easily peeled from the alumina, provided it was at least 4 µm thick and demonstrated selectivities for H_2O over N_2 and O_2 at or near the measurement limit of 10^4 with very high H_2O vapor transport rates (see figure).

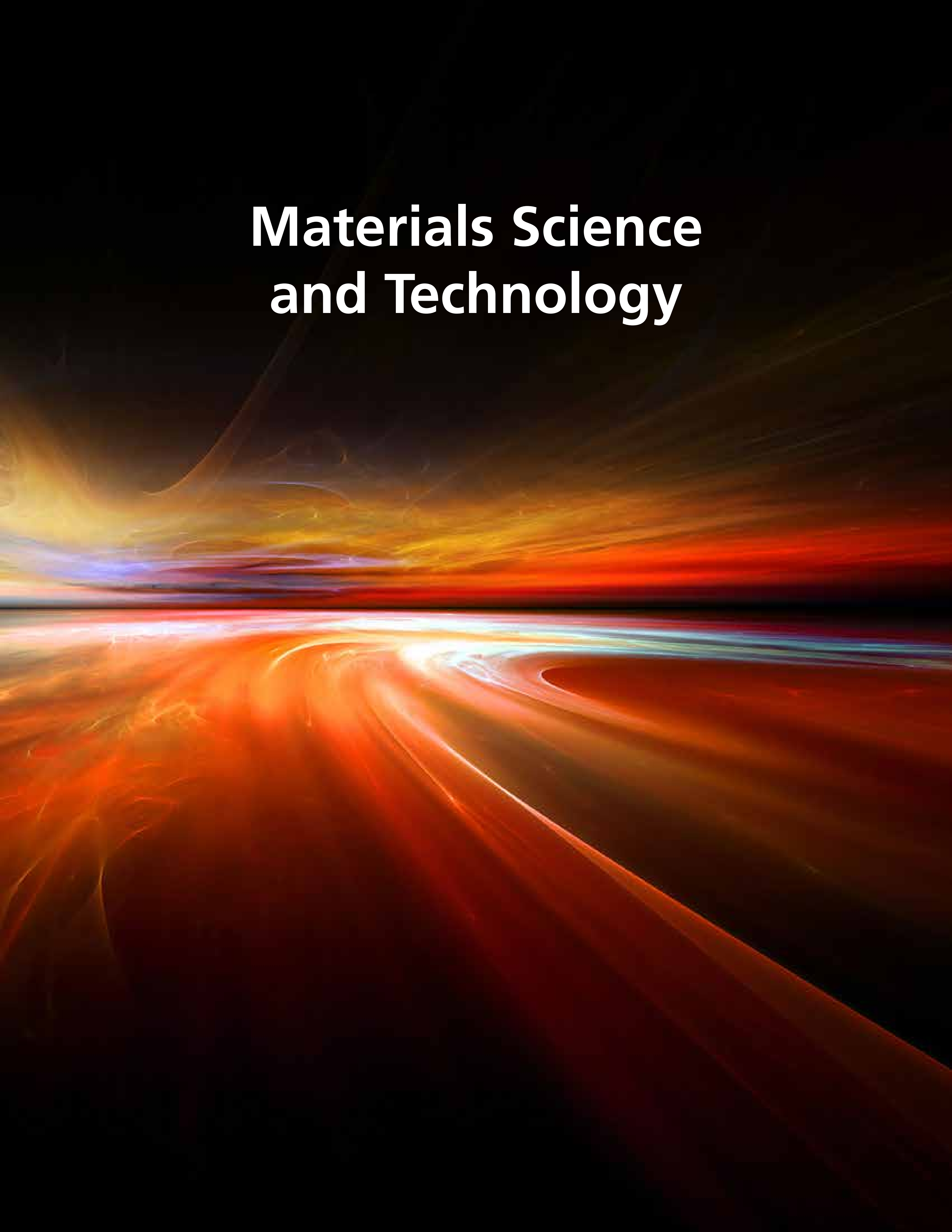
To enable manufacturable membranes, support and protection layers were added. Supported IGO membranes were prepared by drawing the IGO suspension through standard filter paper and both polycarbonate and polypropylene membranes. The filter paper roughness was too high and disrupted the IGO membrane, but both polymer-supported membranes were functional and observed as susceptible to temporary disruption due to liquid water accumulation on

PN12022/2423

their surface. This led to penetration by both N_2 and O_2 permeation, though the high selectivity returned once the liquid water was eliminated. To provide a protected film for manufacturing operation, IGO membranes were prepared with permeable surface coating. This membrane showed acceptable transport rates and did not exhibit liquid water disruptions.

In summary, we demonstrated that GO based membranes could be successfully integrated into multilayer structures to provide high selectivity, high permeability and the potential for manufacturable processing as long as the support structure was sufficiently smooth. The addition of a surface coating improved the robustness of the device operation in conditions where liquid condensation could occur.

Materials Science and Technology



Advanced Sorptive and Signature Indicating Materials for Ultra-Trace Detection

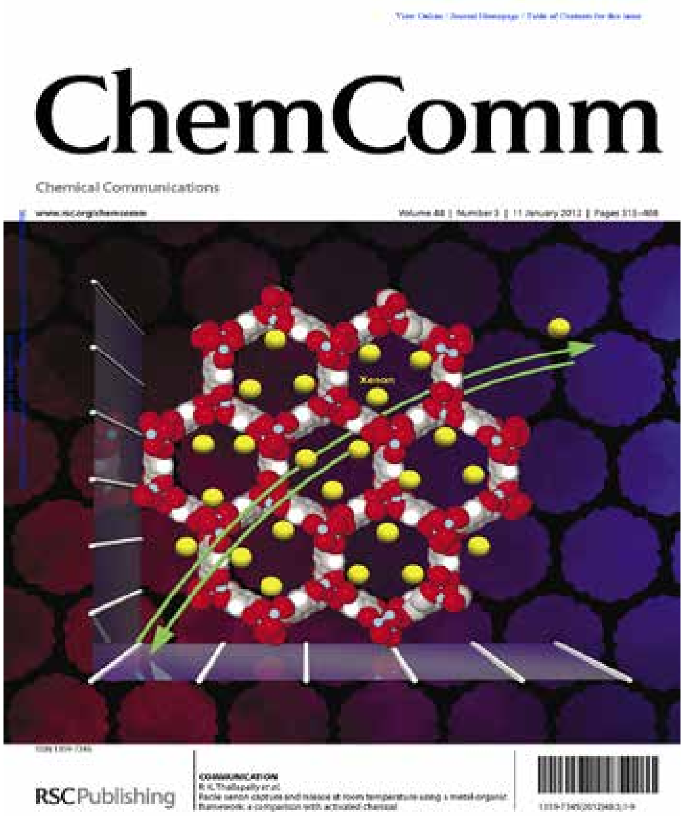
Jay W. Grate

> ***The collection and detection of signatures of undeclared nuclear activity is an essential technical capability for monitoring treaty compliance.***

Signatures of nuclear activities can occur in the gas phase as gaseous molecules or aerosol particles, in the liquid phase as dissolved ions, or as residues or components of solid samples. This project will develop three different but complementary technologies for concentrating and detecting signatures. Under the first task, we select and synthesize appropriate metal organic framework (MOF) candidates that are relevant to xenon gas sorption, collection, and separation. The second task is about enhancing signatures of a wide variety of dissolved or suspended nuclear materials, fission products, and related process chemicals in water or other liquids. The third task involves the design of uranyl ion binding TCC-cpGFP proteins for engineering sensors capable of uranium detection for treaty monitoring applications. These tasks and their specific project progress are described below.

Metal Organic Frameworks (MOFs) for Noble Gas Sorption. With regard to the gas phase, the collection of xenon gas is an important aspect of treaty monitoring and detection of undeclared nuclear explosions. Sorptive materials play a key role in this collection. This project addresses a new type of sorbent, MOFs, with superlative properties compared with current carbons and zeolites for gas capture and separations. We are developing and investigating MOF materials for gas collection and separation of xenon. The development of these materials will lead to more effective collection of xenon in the face of variable backgrounds.

We have investigated a number of MOF candidates, starting with the well-known MOF-5, focusing on capture at noncryogenic temperatures. We have found a MOF structure, NiDOBDC, that captures xenon gas with twice the capacity of MOF-5, and which has superior structural stability with uptake and release of guest molecules. The uptake can be further affected by the metal atoms that comprise the MOF. The uptake of xenon by NiDOBDC has been compared with that of activated charcoal, which is a conventional sorbent evaluated for comparison. Neither NiDOBDC nor charcoal has significant uptake for N_2. The uptake of Xe by NiDOBDC is comparable to that of carbon overall, with superior uptake from 0.25 to 1 bar. The calculated weight percentage of xenon at 1 bar, on NiDOBDC was found to be 55 wt% and the desorption was completely reversible. The uptake of xenon by MOF-5 at 1 bar is only 26 wt%, about half that of NiDOBDC. The uptake values for other atmospheric gases such as N_2 (1 wt%) were very small at 1 bar. Further, in addition to providing excellent xenon uptake, the MOF materials provide more facile release of gases than activated charcoal. This feature can be advantageous in technological applications for gas capture, concentration, and release. The energetics of the xenon interaction with NiDOBDC were examined in terms of the isosteric heat of adsorption, and the interaction of the guest xenon molecules with the MOF host surfaces. This work has resulted in a peer reviewed journal article featured on the front cover of *Chemical Communications*.



Sorption of xenon by an MOF as suggested schematically and featured on the cover of *Chemical Communications*.

Magnetically Active Sorbents for Proliferation Signature Collection and Detection. Capture of low concentration signatures, such as radionuclides, heavy metals, and organic compounds from complex matrices and/or large volume samples is challenging. This effort focused upon the development of magnetic nanoparticles for nuclear proliferation signature collection and detection. By modifying the surface chemistry of these high-surface area materials extremely high affinity and capacity sorbent materials can be created. Sorbent performance of the modified nanoparticles far exceeds that of commercially available sorbents for the collection of trace levels of radionuclide. Selectivity and affinity of the nanoparticles can be adjusted with installation of the desired surface chemistry and new materials with extremely high affinities for fission products and f-block elements have been created and demonstrated. The small particles disperse easily in solution enabling rapid collection and concentration. After capture of the target radionuclides the magnetic properties of the nanoparticles allows them to be rapidly separate the nanoparticles from the bulk solution and magnetically direct them into a geometry ideally suited for analysis. We have explored and optimized a range of methods for collection of or trace radionuclides signatures from large volumes. We have demonstrated accelerated assay of the nanoparticles with gamma detectors, beta detectors, alpha detectors counting, proportional counters, liquid scintillation and ICP-MS. Efforts from this project have resulted in 5 peer reviewed manuscripts (to date) and were featured on two journal covers (*Health Physics Journal* and *ChemSusChem*). Patent applications and additional papers are being assembled and submitted based upon this work.

Protein Based Uranium Detection. This task enhances the capability for stand-off detection of upstream uranium processing using novel protein-based fluorescent sensors that bind to uranium species. These proteins were designed to fluoresce only in the presence of labile uranyl species and are being functionally tested for high affinity/specificity to demonstrate effective and enhanced fluorescence detection. Design of the sensor material was based on metal binding trimeric coiled coil peptides fused to circularly permuted variants of fluorescent proteins. Our research used the green fluorescent protein (GFP) because its structural and fluorescent properties have been well characterized. However, the results can also be extended to the design of other novel metal binding fluorescent proteins.

Genes encoding the cpGFP-TCC peptides and controls have been synthesized and incorporated into both yeast and bacterial surface display vectors. Metal binding on the surface of both yeast and bacteria displaying the proteins have been demonstrated. Initial rounds of directed evolution to alter metal binding specificity have been accomplished and continue to be characterized using iterative rounds of mutagenic PCR. *In vitro* expression of the constructs to produce soluble forms of the sensor proteins were accomplished but the yield of soluble protein was relatively low. Therefore we developed an additional approach to creating metal-specific sensor proteins by starting with a naturally occurring metal-binding protein that we fused to cpGFP to create a protein that fluoresces only in the presence of the metal to which it naturally binds. Eight directed mutations were conducted on the wild-type scaffold to tailor the protein specifically to bind to uranyl ions. This mutated protein was fused to cpGFP to create a protein that fluoresces only in the presence uranyl ions. These sensor proteins are expressed very well in *E. coli* and shown to be active by fluorescence *in vitro*. The fluorescent sensor protein for uranyl ion detection has not been described in the literature and is thus novel.

Development of Graphene/Ionic Liquid Hybrid Material for Ultracapacitors

Vijay Murugesan

The compact and high performing energy storage devices need optimal interfacial regions. This project focuses on developing graphene/ionic liquid-based designer interfaces to achieve high energy density ultracapacitors.

The interaction between a charged surface (an electrode) and ionic solution an electrolyte) is pivotal to the functioning of ultracapacitors. In this interfacial region, ions from the electrolyte can form electric-dipole with oppositely charged electrodes to form an electric double layer capacitance (EDLC) formation. This is the heart of ultracapacitors and leads to many attractive properties, including longer cycle-life (>10,000 cycles) and higher charge/discharge rates. However, the situation also inflicts a serious limitation in energy density due to the absence of optimal interfaces. Because the amount of stored energy is dependent on the surface area of the electrode and the electrochemical stability of the electrolyte, energy density can be increased by employing an electrode material with a higher surface area (i.e., graphene) and an electrochemically more stable electrolyte, such as ionic liquids. Hence, we are designing an optimal interfacial region consisting of exfoliated graphene (G) and ionic liquids (ILs) to achieve ultracapacitors with energy density closer to that of lithium ion batteries.

The major challenge in developing a G-IL nano-hybrid structure is preventing graphene sheet restacking to allow intercalating the ILs in desired thickness between individual graphene layers. Such a process requires controlled interlayer spacing (i.e., IL thickness) and more favorable affinity between the ILs and graphene. To create this optimal interfacial region, it is essential to have a comprehensive understanding of the molecular structure and dynamics of these complex interfacial regions. We performed combined experimental and theoretical analyses to gain molecular level insight into these interfacial region between graphene and ionic liquids.

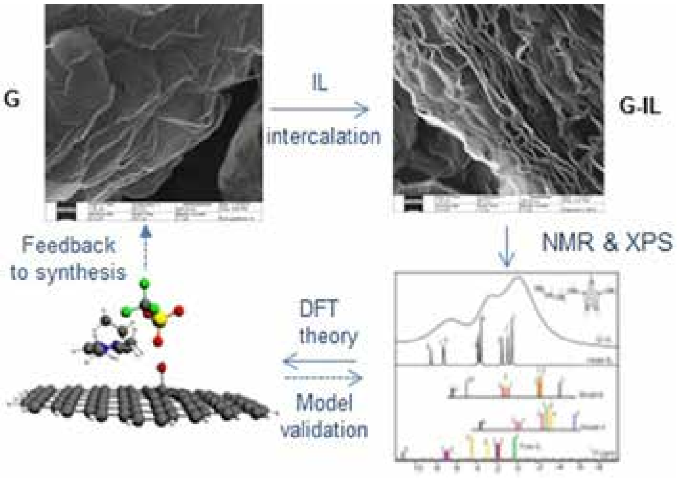
To understand the molecular interaction between the G and IL, a monolayer of 1-butyl-3-methyl-imidazolium ($BMIM^+$) trifluoromethanesulfonate (TfO^-) on graphene surfaces was synthesized (hereafter termed G-IL) using aqueous solution based method. The low molar ratio of G to IL (1:1.5) used in this synthesis and the extreme solubility of IL in water ensures the formation of IL monolayer on graphene surface. This formation enabled us to study the molecular level interaction between graphene and IL. Subsequently, nuclear magnetic resonance (NMR), x-ray photoelectron (XPS), and infrared (FTIR) spectroscopy analyses on this G-IL material were carried out. These analytical results are then correlated with molecular models, which were derived using density functional theory with empirical dispersion correction (DFT-D3) based methods.

This combined approach sheds light onto the G-IL interfacial region, and the results can be summarized as follows:

- BMIM cations can interact with functional groups on the graphene surface just as they interact with defect-free graphene regions, whereas TfO anions are repelled by oxygen containing defect groups (i.e., hydroxyl and epoxy)
- BMIM cations orient parallel to the graphene layer from π-π stacking interaction to form a primary interfacial layer subsequently capped by TfO anion layer.

Based on this information, restacking of graphene sheets is prevented by incorporating epoxy and hydroxyl groups on the surface. This leads to successful integration of graphene and Ionic liquid into a nano-hybrid structure with optimal interfaces and desired spatial separation (<10 nm).

As a next step, we will focus on testing various ILs compositions in G-IL nano-hybrid material for better electrochemical cycling properties and provide input for tailoring ILs in the G-IL optimal interfacial design process. Further, we will develop unique probe systems to perform high resolution *in situ* NMR and XPS spectroscopy to test these G-IL materials during charge/discharge cycles. These efforts will ultimately lead to high energy density ultracapacitors with optimal designer-interface materials.



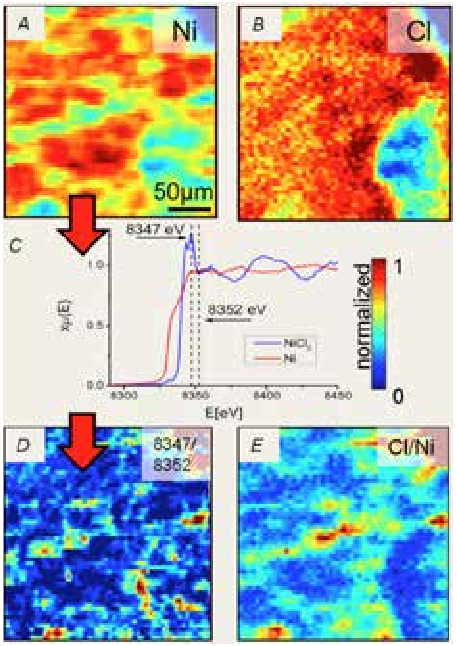
G-IL hybrid nanostructure with optimal interlayer spacing is achieved through fundamental understanding of interaction between ionic liquid molecules and oxygen containing functional defect groups on graphene surfaces.

Development of Hard X-Ray Emission Spectroscopy Nanoprobe

Nancy J. Hess

> ***We are developing an in situ probe of the electronic structure of battery materials during operation to gain fundamental knowledge of irreversible transformations that impact battery performance.***

Battery lifetime and performance can be improved by elucidating mechanisms that lead to irreversible transformations and changing electronic structure. Much of the previous work on battery materials relies on *ex situ* measurements and less direct measurements of electronic structure with lower spatial resolution. Understanding the detailed electronic structure of multivalent ions is fundamental to many fields of chemistry and materials engineering, particularly in energy storage and materials. X-ray emission (XES) is complementary to x-ray absorption spectroscopy (XAS) in that it provides element-specific measurement of oxidation state, bond length, and neighboring ligand identity. However, unlike XAS, XES is a "more local probe" of the electron-electron interactions, so it gives more detailed electronic structure information such as orbital splitting, spin state, magnetic properties, and bond character and is less influenced by structural disorder and thermal effects. Through the use of low-cost, element-specific XES spectrometers, we will construct a modular system capable of investigating the electronic structure of the transition metal, lanthanide, and light actinide elements within a variable temperature sample environment and with spatial resolution ultimately at the nanometer scale.



A and B are Ni and Cl fluorescence maps of Na/$NiCl_2$ battery, respectively. C shows normalized XANES for Ni and $NiCl_2$. D maps the Ni ratio at 8347 to 8352 eV. E shows the ratio of the Cl to Ni at 8352 eV for comparison.

We obtained chemical maps of Na/NiCl (ZEBRA) batteries in fully charged and discharged states cycled at high and low currents using x-ray absorption near edge spectroscopy (XANES) at sector 20 the Advanced Photon Source. We observed segregation of Fe from Ni in the discharged states of these batteries (in the charged state Fe and Ni were approximately co-located). This segregation was more pronounced in the battery cycled at high current, and therefore may be related to the diminished performance under these conditions. The Fe XANES spectra of the battery cycled at low current were predominantly iron metal, but the spectra from the high current battery were significantly different and did not match any of the standards we anticipated (Fe, Fe_2O_3, $FeCl_3$, FeS). Our best candidate is Na_6FeCl_8 that would indicate a reaction with the molten salt electrolyte, and we are seeking reference spectra for this compound.

The Ni XANES spectra were all consistent with Ni metal or $NiCl_2$, in agreement with the expected battery chemistry. By combining maps taken at different incident energies corresponding to regions of the XANES spectra characteristic of Ni and $NiCl_2$, we were able to produce a chemical map of $NiCl_2$. This was much more informative than the elemental maps of Ni and Cl alone, identifying small grains of $NiCl_2$ and their interface with Ni.

In collaboration with the University of Washington, we constructed Ni XES spectrometers in both miniXS and polycapillary designs. Ni K-beta spectra were recorded from the Ni battery sample at sector 20-ID with a peak intensity over 9000 counts/s. This demonstrated the suitability of the concept at the x-ray flux of beamlines with a higher resolution.

The next step in our research project is the construction of a sample environment for the *in situ* operation of a Na-$NiCl_2$ BASE battery. We plan to modify an existing design from the Stanford Synchrotron Research Laboratory (SSRL) research team. The SSRL thin film battery is designed for transmission XAS experiments and is well-suited for incorporation into the miniXS spectrometer.

PN12024/2425

Facet Specific Chemistry of Noble Metal Nanoparticles Using an Enhanced Scattering Infrared Scattering Near-Field Optical Microscope

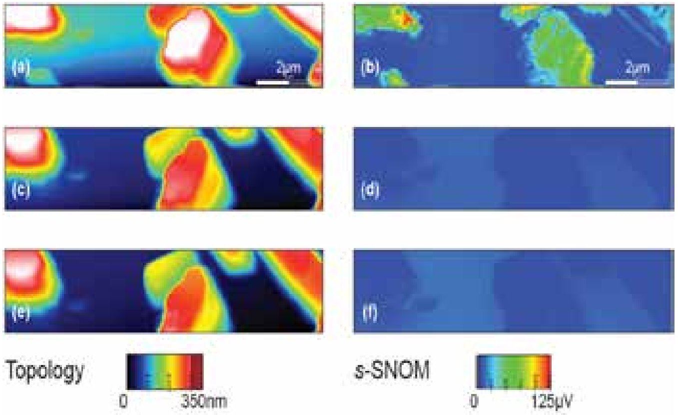
A. Scott Lea

> ***We are adding a new capability to existing equipment that allows investigation of reactive sites on various faces of crystalline nano-sized noble metals and the physical processes that occur in nanostructured materials.***

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 with one exception, none is broadly tunable over a large spectroscopic range nor has resolution that approaches 10 nm.

This project will 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 investigate the distribution of bonding configurations and heat of adsorption of probe molecules on different crystal facets of noble metal nanoparticles. We are working to establish an inelastic electron tunneling spectroscopy (IETS) capability on EMSL's low-temperature scanning tunneling microscope (LT STM) that will provide spectroscopic information about individual species involved in surface-mediated reactions at the atomic level. 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), the range of many fundamental vibrational bands. ECQCL's rapid scanning capabilities 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.

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} in FY 2011. To demonstrate the integration, we identified an experimental system with nm- to μ-size spatial variability in its infrared absorbance between 1280 cm^{-1} and 1380 cm^{-1} and selected polymer co-blends composed of polyethylene and polyethylene oxide (PE/PEO) that phase separate at room temperature.



AFM tapping mode topography (a, c, and e) and the corresponding 2Ω scattering SNOM signals (b, d, and f) for crystals of pentaerythritol tetranitrate deposited on gold. For the 300 nm high crystals, contrast in the 2Ω SNOM signal is observed when the IR light is tuned to the resonance of the nitro group (b at 1270 cm^{-1}) but not at wavelengths off-resonance (d and f).

In FY 2012, the s-IR SNOM system was disassembled, transported to PNNL, and re-assembled and qualified for operation with the femtosecond laser system and ECQCL. For the C-O adsorption experiments on noble metal nanoparticles, it is critical to have laser tunability in the 5.0–5.4 μm wavelength range. We purchased a 5.02–5.52 μm ECQCL and have successfully integrated it into the s-IR SNOM instrumentation and have demonstrated field enhancement of the second harmonic (2Ω) scattering SNOM signal imaging slot antennas etched in a gold film deposited on potassium bromide. Additionally, we utilized ECQCL spectroscopically to image the spatial distribution of nitro group containing molecules on the surface of gold using IR wavelength tuned to the oscillator. We also had an environmental chamber machined that conducts CO adsorption experiments on Pd nanoparticles.

We have incorporated the inelastic electron tunneling spectroscopy into the LT STM and have developed a detection technique on the basis of sample bias voltage modulation and lock-in amplifier will be developed to greatly improve a signal-to-noise ratio of IETS spectra. We also began configuring the system for initial experiments comprised of recording single-molecule vibrational spectra of O_2, OH, and H_2O on $TiO_2(110)$.

PN11035/2357

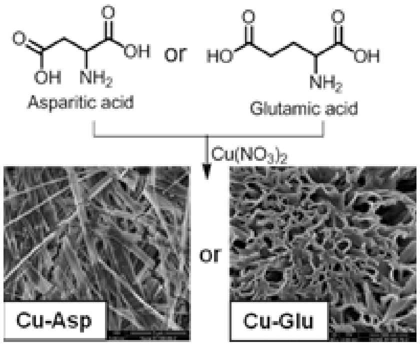
Hybrid Electrodes for Next Generation High Energy Ultracapacitors

Satish K. Nune

We are developing solution-based strategies for carbon architecture synthesis with large surface areas and controlled pore distribution for improved mass/charge transfer properties from an enhanced electrode/electrolyte interface.

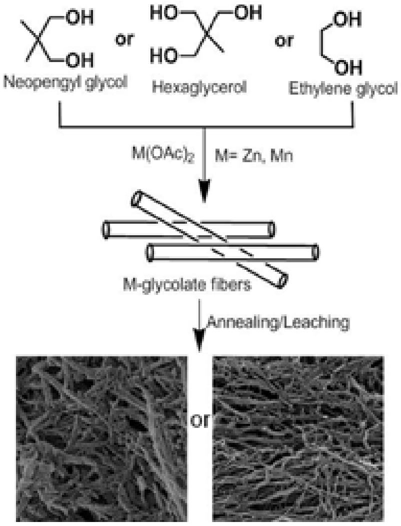
Supercapacitors with high power and energy densities in combination with batteries serve as potential alternatives to increase energy densities while providing high power performance. Carbon nanotube (CNT) and graphene nanosheets (GN) materials with outstanding properties including high surface area, thermal conductivity, and stability have been used as a candidate material. However, the energy density of existing state-of-the-art capacitors is an order of magnitude lower than metal hydride and Li-ion batteries. GN tends to aggregate and stack in multilayers from vanderwall interactions affecting performance, high cost of CNTs, and limited functionalization strategies limiting their use. Inexpensive mesoporous carbon fiber-based electrode materials with efficient ion diffusion pathways serves as potential alternative. The key scientific barrier for low capacitances with fibrous materials is poor accessibility of electrolytes to electrodes. Understanding fundamental mechanisms and properties required for improved performance enables modification of synthesis strategies that offer electrode materials with enhanced electrode/electrolyte interfaces. Characterization and electrochemical measurements of synthesized materials will advance our understanding of fundamental mechanisms for improved performance reducing American dependence on foreign energy (oil) imports

In FY 2012, we synthesized and characterized carbon materials using three different strategies: self-template by solution growth pathway, hydrothermal carbonization, and modified aerogels process. Room temperature preparation of carbon materials by solution grown self template consists of forming glycolate and carbonization/leaching, resulting in fibrous materials. Our method does not require any external hard templates. We also successfully synthesized Cu-aspartitic/glutamic acid nanofibers with 100–200 nm diameters in aqueous conditions. We hypothesize that the initially formed Cu-aspartate acts as an *in situ* template during the carbonization process. Even the carbonization of Cu-aspartate and glytamate resulted in carbon architectures with low surface areas, clearly indicating that fibrous framework of these materials is not retained. We theorize that the thermal treatment of fibers resulted collapsing of framework by the loss of coordinated solvent molecules.



Synthesis of Cu-amino acid fibers

In another task, we successfully developed a new approach to synthesize carbon materials with large surface areas (e.g., 2028 m^2/g) using ethylene glycol or neopentyl glycol or 1,2 hexadecane diol as structural constructors. We hypothesized that by varying carbon chain length and steric bulk in these constructors, we could potentially synthesize high surface materials with control over pore size distribution for enhanced electrode/electrolyte interaction resulting improved energy densities. In the second approach, we used hydrothermal carbonization route to obtain carbon materials at elevated temperatures (180°C). We used carbohydrates (glucose) and aminoacids (cysteine) as structural constructors. Microspheres were obtained by the reaction of cysteine amine and glucose aldehyde groups, followed by subsequent dehydration and polymerization. BET surface area of the solid obtained after pyrolysis at 900°C is 379 m^2g^{-1}. In the third method, we developed new approach to coat metal oxides on carbon materials in single step using modified process used for aerogels. However, coating metal oxides resulted in significant reduction of surface areas (1125 to 118 m^2/g) and pore distribution.



Carbon fibers obtained using glycols

We successfully synthesized carbon fibers with high surface area and acquired 8-channel potentiostat. We are well-positioned in FY 2013 to perform electrochemical measurements on synthesized materials with high surface areas. We will investigate the role of metal oxide on capacitance, micro/mesoporosity of electrode materials, and the chemistry of high voltage electrolytes on performance. In addition, we will use elelectrochemical deposition of metal oxides in the presence of carbon-based material or permanganate reduction followed by carbonization.

Imaging the Nucleation and Growth of Nanoparticles in Solution

Ayman M. Karim

This project is developing in situ characterization tools for imaging the synthesis of nanoparticles in solution. Direct real time visualization would allow a fundamental understanding of synthesis mechanisms and therefore accelerate synthesis development to make materials with specifically engineered nanostructures for a wide range of energy storage and conversion applications.

The synthesis of nanoparticles in solution is the most promising, tunable method but is not well understood due to the difficulty of experimentally observing the nucleation and growth processes. Consequently, most synthesis efforts rely on trial and error from the lack of a fundamental understanding and paucity of *in situ* characterization tools. Our goal is to develop new *in situ* tools for imaging the nucleation and growth of nanoparticles in solution by combining microfluidics, x-ray absorption spectroscopy, and atomic-resolution aberration-corrected transmission electron microscopy. The project will result in an *in situ* microfluidic cell and development of data collection and analysis techniques for the study of nanoparticle nucleation and growth with millisecond time resolution using synchrotron techniques and *ex situ* atomic-resolution aberration-corrected transmission electron microscopy.

A novel microfluidic silicon/pyrex reactor for Pd nanoparticles synthesis was designed and fabricated. Most microfluidic reactor designs reported in the literature for nanoparticles synthesis mix the reactants at the reaction temperature. The disadvantage of mixing the reactants at the reaction temperature is not knowing the exact concentrations during the reaction while the reactants are not fully mixed.

The design has two unique features:

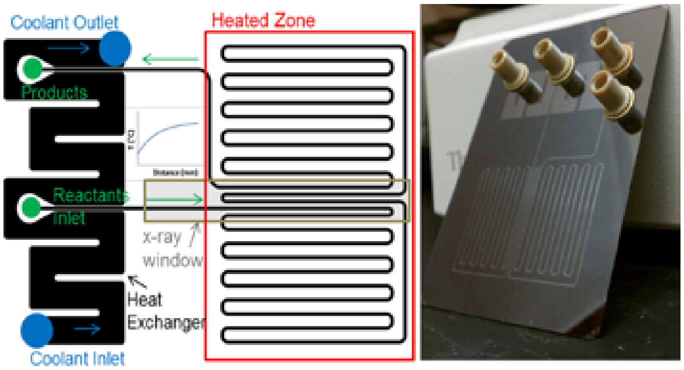
- A heat exchanger at the inlet keeps the reactants at low temperature (where the reaction rate is negligible) until fully mixed. This allows for controlled heating and, more importantly, provides a known concentration and temperature at each point in the inlet channel.
- An isothermal heated zone consisting of a long serpentine channel where the x-ray window covers the inlet, middle two, and outlet channels.

This design allows us to analyze the nanoparticles nucleation at millisecond time resolution in the inlet channel as well as the growth of the nanoparticles at minutes time scale in the middle and outlet channels.

Preliminary results for the synthesis of Pd nanoparticles in the microfluidic cell revealed that visible light has a strong effect on the nucleation and growth kinetics at room temperature. Increasing the synthesis temperature resulted in smaller Pd nanoparticles with narrow size distribution.

The narrow size distribution Pd nanoparticles provided a model system to study the stability and growth mechanisms by *in situ* TEM. The results showed, for the first time, a direct evidence of atomic migration between particles leading to anomalous particle growth. The work has been submitted to a special issue of *ACS Catalysis*.

The work in FY 2013 will be focused on synchrotron studies to understand the effect of temperature, reducing and capping agents on the nucleation and growth mechanisms of Pd nanoparticles. The microfluidic reactor design will also be modified to allow the characterization of other metals that require lower x-ray energies than Pd (e.g., Pt, Au, and others), which requires thinner windows.



Microfluidic reactor for millisecond time-resolved x-ray absorption spectroscopy studies of nanoparticles synthesis. The heat exchanger at the inlet and the heaters by the serpentine channel allow for two temperature zones and a well-defined t_0. The x-ray window covers the inlet, two middle, and outlet channels, which allows for millisecond time resolution during the nucleation and up to minutes time resolution during the growth.

Integrating Multimodal Chemical Imaging Instrumentation by Data Reduction and Resolution Merge

Dongsheng Li

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.

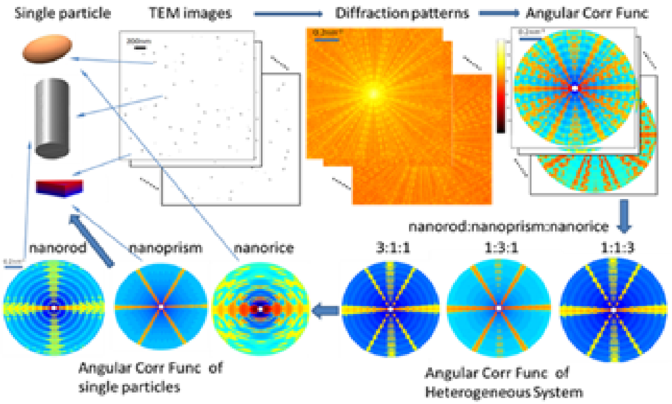
Image integration for chemical imaging instrumentation must be advanced to meet the development of large data-set generated at high speed typical in light source chemical imaging instrumentation. This trend is also observed in our in-house imaging facility development, such as high resolution mass spectrometry, 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.

To attempt making the impossible possible, we are developing the ability to simulate a large, high-resolution image based on a single coarse and several small, high-resolution images. The resulting revised image would help researchers identify the "hot spots" where complex chemical or mechanical phenomena are likely to be occurring. Drawing on exascale computing, this new model would make it possible for multiphysics, multiscale simulation ranging from nanometer scale to meter scale. Collectively, these high-resolution images that cover large areas of a sample provide a complete, detailed view of complex, heterogeneous structures with value to energy production, environmental remediation, and pharmaceutical innovation.

In FY 2011, we started with a low-resolution, low-magnification optical microscopy image and multiple high-resolution, high-magnification scanning electronic microscopy 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 was investigated, with information from low-resolution images serving as input to reconstruct the high-resolution image.

In FY 2012, we focused on image reduction to retrieve interesting statistical information to determine structure. We used the ring angular correlation function, a characteristic feature determined by the particle structure. Averaging over a large number of ring angular correlation functions calculated from x-ray diffraction patterns canceled cross-correlations between different particles and converged to autocorrelation functions of single particles. Applied on heterogeneous disordered ensembles, the retrieved function is a linear combination of single-particle autocorrelation function multiplied by molar ratios in a heterogeneous system. Using this relation, the ring angular correlation functions of the individual component particles in the heterogeneous system can be retrieved through the high throughput fluctuation x-ray scattering technique. As demonstrated in the figure, component structure of a simulated heterogeneous system composed of nanorods, nanoprism, and nanorice was determined using this method.

In FY 2013, we will apply the developed capabilities to the analysis and visualization of *in situ* and *ex situ* chemical imaging instrumentation results to deliver a fully operational analysis pipeline on imaging integration. Later, we will integrate the developed techniques with other components of large-scale data management and analysis.



Scheme of single-particle structural determination from heterogeneous ensembles using the fluctuation x-ray scattering technique.

Integration of Molecular Imaging Techniques to Probe the Photoinduced Charge Transfer in Semiconductor Quantum Dots-Polymer Hybrid Solar Cells

Dongsheng Li

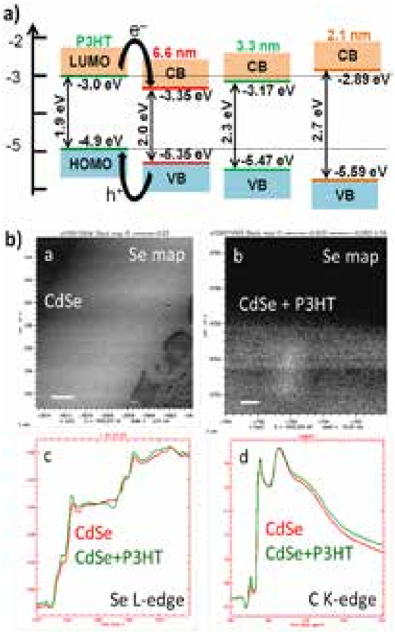
We are developing a novel integration of molecular imaging and spectroscopy capabilities that will advance the fundamental understanding of the photo-induced charge transfer in hybrid solar cells.

In semiconductor quantum dots polymer hybrid solar cells, the chemical interaction between quantum dots and polymer matrix is a key element 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 photo-induced 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 will 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.

We studied the structure-property relationship and 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. 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. This also results in severe agglomeration of QDs.

We established the band alignment of P3HT with CdSe quantum dots of various sizes to establish the size dependent charge transfer between them. We also performed high resolution TEM and helium ion imaging of individual CdSe quantum dots prior to and after incorporating these in P3HT matrix. Results from these techniques highlight the strength of these techniques and challenges in chemical imaging of individual quantum dots at extremely small length scales. In addition, we collaborated with Canadian Light Source for STXM analyses of the CdSe QDs and following interaction with P3HT.

STXM images depicted the agglomeration tendency of the CdSe QDs in P3HT compared to the as-prepared CdSe QDs. Imaging of individual nanoclusters in the as-prepared CdSe QDs was limited by STXM resolution. We are in the process of adopting better sample preparation methods for STXM imaging to obtain in-depth information. The Se L-edge absorption spectra show no significant difference between the as-prepared CdSe QDs and CdSe QDs with P3HT suggesting weak interactions between the P3HT and CdSe QDs possibly from the presence of hydrophobic HDA ligands capped on the CdSe QDs. The C K-edge absorption spectra show an enhanced intensity in the pre-edge region for CdSe QDs with P3HT suggesting the presence of excess carbon from the P3HT. Further analyses of the existing data and experimentation of the new samples are in progress.



a) Band alignment of various sizes of CdSe QDs and P3HT depicting the driving force of charge transfer b) STXM maps and absorption spectrum from QDs a) before and b) after mixing with P3HT.

Both STXM and HIM images confirm our previous observation of agglomeration of CdSe QDs in P3HT and demonstrate the necessity to understand the homogeneous distribution of CdSe QDs in P3HT and their molecular level interactions in the hybrid solar cells.

PN12044/2445

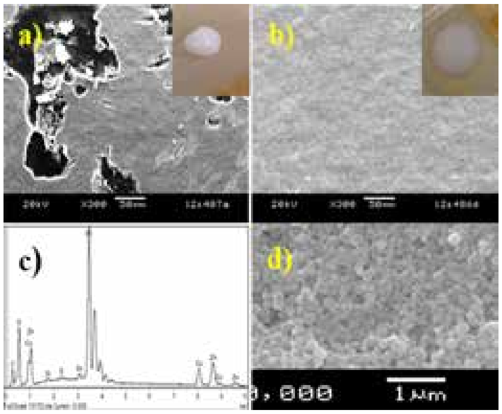
Materials and Methods for Low Cost Photovoltaic Manufacturing

John P. Lemmon

Developing new solution-based thin film photovoltaic (PV) manufacturing methods vs. current costly high vacuum processes is significant to decreasing our nation's dependence on petroleum imports while reducing carbon emissions.

PV cells based on thin film copper-zinc-tin-selenide (CZTS) composed of earth abundant materials have emerged as a potential replacement for one of the leading contenders for thin film solar technologies, copper-indium-gallium-selenide (CIGS). Recently, CZTS demonstrated 11% efficiency in the small cell configuration, which is closer to the record of CIGS. Despite offering great promise, CZTS's complicated nature renders the deposition process complex, time consuming, and costly. Two attractive approaches to decreasing production cost are developing green synthesis of non-vacuum solution based CZTS and applying a superstrate configuration into cell. The goal of this project requires new discoveries to meet aggressive performance targets.

Develop metal hydroxide nano-inks and deposition techniques that produce thin film CZT hydroxide with target composition, thickness, and uniformity. We reported in FY 2011 a process to synthesize inks containing encapsulated metal nanoparticles of copper, indium, and gallium from low cost inorganic salts using a high vapor pressure solvent that evaporates evenly during thin film deposition. Using a high vapor pressure solvent also allowed for spray deposition that has produced uniform films. In FY 2012, we further developed aqueous inks containing Cu-Zn-Sn(OH)_6 (CZT) submicron particles from a low-cost, low-temperature hydrothermal process to minimize the use of organic solvent and reduce experiment requirements. A key challenge was achieving uniform coating on the substrates using the aqueous ink. However, by surface modifying substrates, we produced crack-free, uniform thin film from aqueous CZT inks.



CZT particles ink deposited on ZnS (a). b) and d) show PEI modified ZnS substrates, and insets reveal contact angle differences of droplets. c) shows EDX confirm the composition of Cu, Zn, and Sn.

Optimize selenization condition to achieve desired CZTS films without influencing the superstrate. Previously, H_2Se vapor was used to promote grain growth and selenization rate. However, H_2Se vapor is not only highly toxic (and must be handled using appropriate protective equipment) but also reacts with metal contacts and deteriorate device performance. We applied Se vapor to the process on superstrates to address this issue and optimize experimental conditions. Selenization in FY 2012 led to dense absorber films with ~5μm thickness amenable to further PV cell workup.

Build a small-scale CZTS superstrate cell using solution-based CZTS methods. Pervious results from FY 2011, CdS window layer and high performance TCO layer have been successfully deposit on the substrate. Based on the similar approach, significant progress was made toward fabrication and performance evaluation of full superstrate PV cells generated from Phase I materials. Full cell fabrication and performance tests have been conducted. Although the resistance is high, these represent our first attempts to produce full CZTS PV cells from superstrates. The high resistivity could be explained by the film microstructure, where small grain size and voids are generated in film during selenization that hinder electron transportation. The program is now focused on optimizing thin film processing to yield higher efficiencies and to develop large format cells.

Left: as deposit CZT superstrate; middle: after selenization; right: full PV cell with gold electrodes.

An *in situ* optical reactor using a sapphire window for monitoring chemical reactions and processes with a 3–5 µm thermal imaging camera was developed to monitor real temperature changes from free energy differences in chemical reactions or emissivity changes in reaction surfaces for new product formation. In addition, a turnkey PV performance measurement system was purchased to replace an inaccurate, outdated system that yielded highly irreproducible results. The new capability will allow for publication of performance data and accurate communication with potential PV clients.

In FY 2013, the program moves into Phase II, where the CZTS microstructure will be further optimized and performance tested in PV cells to determine overall efficiencies and cost impacts.

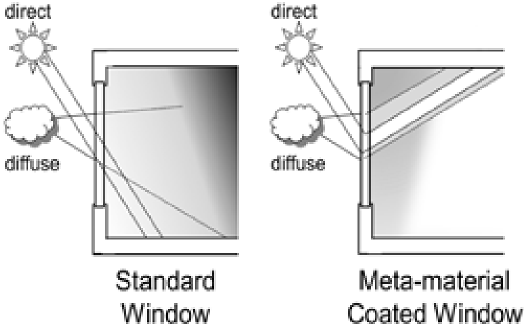
Meta-Material Coatings for Daylighting Windows

Kyle J. Alvine

This project is developing low cost advanced window glass coatings to bring daylight significantly further into buildings to offset artificial lighting energy use. If successful, this new technology is projected to save up to 0.66 quadrillion BTUs of energy and offset nearly 11 million tons of carbon per year over standard daylighting window systems.

The ability to tailor the redirection of light through innovative low-cost nanostructured meta-material coatings would significantly reduce energy consumption for building lighting using passive 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 the potential to save 1 quad of energy. The ability to redirect light even further into a building to 30 feet with potentially low-cost nanostructured coatings could almost double the energy savings. This would be a proverbial game-changer for building energy usage. Thus, the overall objectives of this project are to demonstrate the proof-of-concept of nanostructured coatings to redirect light, and to accomplish this challenge over the full visible spectrum. The approach used a synergistic combination of modeling and fabrication efforts to deliver rapid results.

In FY 2011, nanofabrication tools and experience were developed to fabricate the appropriate nanostructures. Complementary numerical modeling simulations were performed to predict the response of these nanostructures. In addition, an optical spectrometer was employed that could measure both the transmission and full scattering response from fabricated structures. Also in FY 2011, preliminary structures were fabricated that demonstrated a strong resonant dip in transmission as expected for single wavelength structures. Modeling results showed that significant light redirection was possible from these types of nanostructures.



Schematic comparison of daylighting from a standard window (left) to a meta-material coated window (right).

In FY 2012, the project was focused on demonstrating both with modeling and experiment that fabrication of nanostructures capable of a broad-band spectrum response across the full visible light spectrum is possible. The response is critical to optimal performance by creating structures that redirect light over the full visible or white-light spectrum for accurate color rendition. In addition, some effort during the current fiscal year was redistributed toward improving the optical scattering measurement setup for improved collection performance.

To achieve this goal experimentally, new types of nanostructures that were predicted to be capable of light redirection over a broad range of wavelengths from 400 nm up to 750 nm were fabricated through a combination of self-assembled nanotemplating and metal sputtering. These structures were based on designs developed in FY 2011 and guided by complementary modeling efforts in FY 2012. Multiple test samples between 1″ × 1″ and 1″ diameter were fabricated using this new self-assembly process. Significant effort was put into developing this fabrication technique with a high lateral packing ratio of the structures to improve performance. There is still room for substantial improvements in lateral packing and defect reduction.

These test samples were subsequently measured with the optical scattering setup and showed a broad-band response from approximately 500 nm up to 1100 nm. This response covers roughly 70% of the visible light and a substantial portion of the near infrared light spectrum as well. While further refinements are needed to improve light redirection performance and to shift the response to the blue region of the spectrum, this novel result nonetheless demonstrates that broad-band response is possible with these structures. Complementary modeling efforts were also used to guide the design of the structures described above and showed that they should allow for light redirection over the full visible light spectrum.

Additional future work is needed to bridge the gap between the predicted redirection performance from numerical modeling and the current performance of the fabricated structures. Several areas have been identified for improvement to elicit improved response: defect reduction, improved conduction of metallic coating, and improved packing density. Future work will address these issues with numerical modeling used as a guide to rapidly improve light redirection performance. Overall, the outlook for this novel technology is very promising.

PN11051/2373

Multiphysics Capability Development and Application to Magnesium Alloys

Erin I. Barker

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 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 to 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, creating a much-needed capability at PNNL in 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 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.

For FY 2012, updates were made to FEAWD (Finite Element All-Wheel Drive), including performance enhancements, additional material models, and modifications to the input and output file formats. A parametric study of the impact of texture was completed that quantified the impact of variation in texture to the global response of the sample. A series of statistically equivalent but individually specific textures were utilized. Stronger textures resulted in more variation in the stress-strain response, indicating that local texture mismatch dominates the overall response. These results were presented at the International Symposium on Plasticity, and a paper discussing these results is in preparation.

The tools used to generate and mesh the polycrystal samples were incorporated in the Visko web framework as a proof-of-concept project to show how the tools can be made readily available to a larger community and improve automation of the process. A paper is in preparation discussing how the tools were incorporated into Visko and how combining Visko with scientific tool packages can lead to a better analysis of results.

PN10060/2302

Multiscale Modeling of Energy Storage Materials

Maria L. Sushko

We are developing a hierarchical multiscale simulation technique and novel efficient open source software for modeling charge transport in energy storage materials and performing first-ever simulations of collective charge transport dynamics from atomic to micron scales for coupled ion and electron transport in polycrystalline metal oxide electrodes. A deep understanding of the basis for ion and electron conductivity would guide novel electrode material design with significantly enhanced performance.

Nanostructured transition metal oxides are disordered heterogeneous materials that are difficult to probe at a fundamental level yet appear to hold great promise as energy conversion substrates and energy storage devices such as Li^+ batteries. It is thought that nanostructured electrodes yield improved conductivity and cyclability performance relative to bulk materials due to higher interfacial contact areas between electrolyte and electrode and shorter solid-state diffusion distances for lithium ions and electrons. However, improved overall performance is not universal, and there is currently no theoretical framework to guide optimization strategies. Improved predictability remains complicated by major outstanding unknowns, including poor understanding of nanosizing effects on electrode-electrolyte interfaces and a complex interdependence of electrode materials and electrolytes, contact areas, and diffusion distances, which in turn are linked to diffusive charge transport properties of metal oxides, grain sizes and boundary properties, and grain network properties such as density and porosity. Design principles development for this system is challenging because of the demand to include effects across a wide range of length and time scales.

On atomistic length and time scales, charge-carrying electrons in transition metal oxides are polaronic in nature, and solid-state electron and ion diffusion are subject to strong crystallographic anisotropy and space charge effects, placing unique demands on their theoretical description and computational prediction of their collective transport behavior. The computational methods potentially capable of addressing such multiscale problems fall into heterogeneous multiscale methods. Such techniques have been developed for several types of problems in fluid dynamics and thermo-mechanics. For energy storage devices, several models exist that link microscopic charge transport properties of electrodes with macroscopic performance of electrochemical devices. These codes are based on continuum models such as finite difference, finite element, and phase field models that rely heavily on parameters for electrodes obtained experimentally. This hinders the predictive power of these models as *in silico* design tools for energy storage devices and for novel electrode materials. The latter requires multiscale models linking smaller length scales. However, there are currently no truly multiscale models describing charge transport phenomena from atomistic to micron scales. The project aims to fill this gap and develop the first hierarchical multiscale code for theoretical modeling of energy storage materials.

Our FY 2012 activities focused on three areas: optimizing the performance of multiscale charge transport simulation software based on Poisson-Nernst-Planck/classical Density Functional Theory (PNP/cDFT) software for high performance computing environment; developing a Phase Field model informed by PNP/cDFT for charge transport simulations on a micron scale; and studying the mechanism of coupled ion and electron transport in select metal oxide electrode materials such as $LiNi_{0.5}Mn_{1.5}O_4$ cathodes and TiO_2 anodes.

We developed a parallel processing approach based on PNP/cDFT method for hierarchical multiscale modeling technique for modeling coupled ion and electron transport in nanostructured energy storage materials. The model uses a multiphysics approach where instead of formal consecutive upscaling, we introduce novel types of collective long-range interactions with short-range effects of finer scale models. This model maximizes high accuracy embedded cluster quantum mechanical simulations of elementary charge transport and 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 (10–500 nm) via cDFT coupled with PNP formalism for dynamic effects.

There are two major computations involved in the hierarchical multiscale modeling (i.e., evaluation of chemical potentials of charged species) using the cDFT and solving PNP equations by Newton-Raphson method. To compute efficiently chemical potentials, computational steps were separated into different modules. Redundant computation was removed through modulization, and a parallel version of Picard method of successive approximation is used. For solving equations, modulization steps are employed to remove redundant computation, and a parallel Jacobi method is used. Analysis shows that only boundary values need to be

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communicated between different loops, which makes Jacobi implementation suitable for solving the problem. Possible speeding up strategies of parallel Jacobi method (e.g., successive over relaxation scheme) were also investigated. Numerical results on coupled ion and electron transport in nanostructured energy storage materials using the developed parallel PNP/cDFT method demonstrated the multiscale modeling capability of the developed method. The almost linear scaling of the method with respect to processors in high performance computing environment was achieved.

To improve PNP/cDFT software computing performance, we applied multigrid methods, the most efficient for solving elliptic partial differential equations to solve PNP equations. Numerical results show the implemented multigrid method has close to linear computation complexity with respect to number of unknowns. Results also indicate a more than 20-fold speedup compared to the Jacobi method to achieve results of similar accuracy on a single processor workstation and near linear scalability for number of computing nodes in the HPC environment. The 3D PNP/cDFT code was enhanced with new functionalities that allow simulations in heterogeneous environments such as networks of nanoparticles with anisotropic dielectric constants and diffusivities.

To access larger length scales and include elastic effects, the free energies evaluated on the PNP/cDFT level are used to inform a coarser scale phase field model. The developed phase-field approach investigates the influence of microstructure, thermodynamic, and kinetic properties and charging conditions on charged particle transport in nanocomposite electrodes. Two sets of field variables are used to describe the microstructure. One is comprised of the order parameters describing nanoparticle size, orientation, and spatial distributions, and the other is concentrations of mobile species. A porous nanoparticle microstructure filled with electrolyte is taken as a model system to test the phase-field model. Inhomogeneous and anisotropic dielectric constants and mobilities of charged particles, and stresses associated with lattice deformation due to Li-ion insertion/extraction are considered in the model. Iteration methods are used to find the elastic and electric fields in an elastically and electrically inhomogeneous medium. The results demonstrate that the model can predict charge separation associated with the formation of a double layer at the electrochemical interface between solid and electrolyte and the effect of microstructure, inhomogeneous, and anisotropic thermodynamic and kinetic properties, charge rates, and stresses on voltage versus current density and capacity during discharging and charging.

Application of the multiscale approach to nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathode materials requires a detailed knowledge of the elementary coupled Li^+ and electron transport properties in the bulk material. The role of oxygen vacancies on $LiNi_{0.5}Mn_{1.5}O_4$ ion and electron conductivity and on charge/discharge curves is of particular importance. To this end, we employed molecular mechanics and quantum mechanics simulations to reveal the effect of oxygen vacancies on the structure of $LiNi_{0.5}Mn_{1.5}O_4$ spinel. We showed that for stoichiometric spinel, the lowest energy configuration has higher degree of symmetry ($P4_332$ space group) due to Ni ordering over 4*b* sites, while all other configurations are disordered $Fd\bar{3}m$ spinels with Ni and Mn randomly occupying 16d sites. Moreover, the ordered configuration was 0.4 eV lower in energy than any disordered configuration, suggesting that stoichiometric spinel will have a $P4_332$ structure at room temperature. In contrast, in reduced spinel ordered and disordered configurations occupy the same energy range (i.e., all possible Ni–Mn arrangements become statistically significant). Thus, dominance of a specific type of Ni/Mn ordering in stoichiometric $LiNi_{0.5}Mn_{1.5}O_4$ is lifted once neutral oxygen vacancies are introduced. These results agree well with experimental observations.

Ab initio simulations suggest that formation of neutral oxygen vacancies in $LiNi_{0.5}Mn_{1.5}O_4$ leads to a change of oxidation state of Mn ions adjacent to the vacancy site from 4+ to ~3+ and Ni^{2+} ions to Ni^+ state, which facilitate electron extraction during cathode delithiation. The presence of oxygen vacancies significantly reduces local barriers for Li^+ extraction: due to redistribution of two electrons from the vacancy site onto Ni and Mn cations, the effective electric field at the Li^+ site is reduced. These effects are responsible for low voltage tail on voltage-capacity curves. The concentration of vacancies increases the width of low voltage regions, which explains voltage fade during electrochemical cycling. Understanding voltage degradation offers a way to improve $LiNi_{0.5}Mn_{1.5}O_4$ cathode material performance through controlling crystal stability through nano-structuring or by introducing dopants that increase barriers for electron extraction near oxygen vacancies. These results provide insight into the origin of voltage fade effect, a long-standing problem that hinders commercialization of these promising cathode materials. In addition, multiscale PNP/cDFT simulations for $LiNi_{0.5}Mn_{1.5}O_4$ spinel are underway to reveal the role of nanostructuring and concentration of oxygen vacancies on mesoscopic Li^+ and electron conductivity.

We continued work on an alternative multiscale simulation approach based on the Kinetic Monte Carlo model initiated under a separate project from FY 2010. Using this mode, due to electrostatic coupling between Li^+ and e^-, total conductivity in rutile TiO_2 nanoparticles is determined by the slowest process (i.e., Li^+ diffusion). The coupling effect is responsible for changing the mechanism of charge transport with the contact area between the titania nanoparticle and carbon coating. For full carbon coating, the electrostatic coupling leads to the saturation of surface sites with ions and electrons, which limits overall material capacity. Conversely, localized carbon coating allows for ions and electrons to diffuse well inside the nanoparticle before the onset of strongly correlated flux, which is beneficial for higher capacity and conductivity of nanostructured electrode material. The simulation results could be also of significant importance for the design of nanostructured electrodes with other promising oxide materials for next-generation electrochemical energy storage devices with high-power and -energy densities.

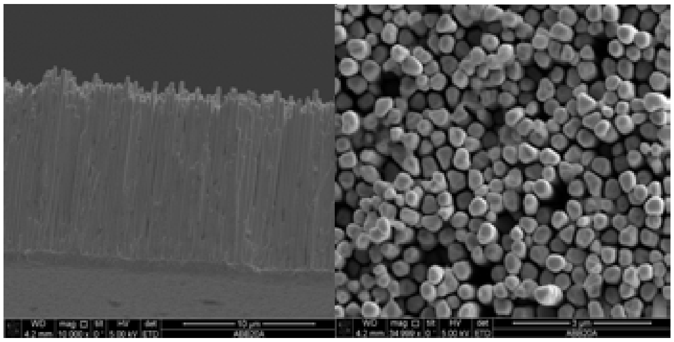
Photocathode Development for Next-Generation Light Sources

Wayne P. Hess

The goal of this project is to produce new photocathode designs to enable the construction of fourth generation light sources at significantly reduced cost and enable the development of ultrafast transmission electron microscopy (UTEM).

Photocathode technology must be advanced to meet the needs of fourth-generation light sources and to develop UTEM. 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, including compact light 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.

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, composite, and plasmonic designs to enable fourth-generation light sources and UTEM. 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 vertical pillar nanostructures (see figure), 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.



Silver nano columns grown electrochemically using anodized aluminum oxide templates. The length and width of columns is controllable.

Developments in 2011 led to considerable progress in FY 2012. For example, we completed construction of a multi-source thin film deposition chamber, and developed the wet chemical methodology for nano-column growth. 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. These accomplishments led to new results, including the silver nanocolumn growth and implanted silver nanoparticles within a MgO matrix using high-energy ion bombardment. Further, plasmonic silver nanoparaticles were formed within the oxide matrix via Ostwald ripening. Next, we were able to measure properties of candidate photocathodes, including electron yield (bunch intensity) and emittance (electron angular distribution). A hybrid photocathode was created, and we conducted XPS and UPS on the hybrid samples. 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 2012, we tested the hypothesis that the quantum efficiency of the hybrid photocathode could be enhanced. The quantum efficiency was enhanced by more than a factor of 20. No loss of photoemission signal is observed after 24 h. A filtered mercury lamp (< 4.1 eV) was used to measure the work function of the hybrid system prior to photoactivation. The work function of crystalline Cu(100) is 4.5 eV. The work function was reduced from that of clean Cu, by over one eV and very large electron yields were produced. The UPS results confirmed the predicted enhancement in quantum yield.

In FY 2012, we initiated *ab initio* modeling of Cu:CsBr and Ag:MgO thin film structures. The electronic properties and energies of the hybrid systems are to be calculated using embedded cluster density functional theory (DFT) and time-resolved DFT. The theory can predict the kinetic energy maximum of Br atoms desorbed following UV excitation. Comparison of the theoretical and experimental results will benchmark the accuracy of the modeling of electronic properties of these candidate photocathode systems. To validate our thin film growth results, experiments were also performed on other hybrid materials. Using angle-resolved UPS, we will measure thermal emittance to demonstrate the utility of hybrid materials. Finally, we will use modeling and photoemission measurements to determine the role of intraband defects.

PN11061/2383

Rare Earth-less Permanent Magnet

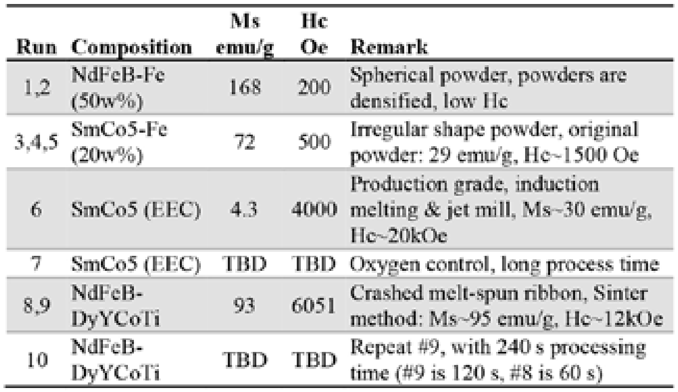
Jun Cui

We are developing a new solid-state consolidation method that will enable the fabrication of next generation magnet material to benefit the United States in both energy security and technology leadership.

With expected growth in electric vehicles and wind energy coupled with limited availability of critical elements Nd and Dy, alternative magnets – either with higher energy product or with reduce rare earth elements (REE) content – are urgently needed. Knowing this, the efficiency of energy conversion is directly proportional to magnet strength. The state-of-the-art $Nd_2Fe_{14}B$ compound exhibits exceptionally high-energy product (58 MGOe) and is widely used for electromagnetic devices. Through creation of nanostructured composite magnets, it may be possible to achieve superior magnetic properties without the need for critical REE. The challenge is to develop a reliable and economical process to produce a 100% dense alloy with nanoscale grains fully aligned and with a uniform soft/hard phase interface. This specific nanostructured architecture has a theoretical energy product more than twice that of the state of the art magnets. However, there is no thermodynamically accessible pathway using the known solidification processes to develop such architecture. Current concepts for solid-state processing have significant challenges due to the requirement of nanoparticle precursors.

The friction stir welding process has been shown to produce fine grains and high degree of texture. It has the potential to be used for fabrication of exchange-coupling nanocomposite magnet. It is the objective of this project effort to prove this concept. The Ames Laboratory and Electron Energy Corporation (EEC) are two collaborators in the effort to provide raw materials and perform EELS-TEM analysis. PNNL's role is developing the friction consolidation process and performing routine characterizations such as x-ray, EBSD, SEM, and magnetometry. With the complexity of processing parameters and a dependence on materials system, it is impossible to have the method fully developed. Our strategy is to gather sufficient evidence and seek DOE support.

Our efforts have focused on answering four questions critical for magnet fabrication: 1) if the processed materials can reach 100% density, 2) if the process can create crystalline texture, 3) if the process can refine the coarse grain from > 1 μm to ~100 nm, and 4) if the process can homogeneous mix the hard and the soft phases without decomposition. Nine experiments were carried out with four compositions. The magnetic properties, microstructure, and phase contents are characterized using VSM, SEM, and X-ray. The results are summarized in the following table.



Run	Composition	Ms emu/g	Hc Oe	Remark
1,2	NdFeB-Fe (50w%)	168	200	Spherical powder, powders are densified, low Hc
3,4,5	SmCo5-Fe (20w%)	72	500	Irregular shape powder, original powder: 29 emu/g, Hc~1500 Oe
6	SmCo5 (EEC)	4.3	4000	Production grade, induction melting & jet mill, Ms~30 emu/g, Hc~20kOe
7	SmCo5 (EEC)	TBD	TBD	Oxygen control, long process time
8,9	NdFeB-DyYCoTi	93	6051	Crashed melt-spun ribbon, Sinter method: Ms~95 emu/g, Hc~12kOe
10	NdFeB-DyYCoTi	TBD	TBD	Repeat #9, with 240 s processing time (#9 is 120 s, #8 is 60 s)

Several processing parameters were found having effects on microstructure and consequently affecting magnetic properties of the resulted samples: plunge loads, rotation speed, processing time, ambient environment, powder size, and shape. In FY 2012, we investigated two parameters: particle size/shape and processing time. We found that irregular shape with sharp edge is preferred over sphere, larger particle size (50~200 μm) is preferred over smaller particles, and longer processing time (> 240 s) produces heavier texture. To date, the sample with the best magnetic properties is from Run 9. Its magnetization is close to the benchmark prepared using the conventional sintering method. Its coercivity is 6 kOe, a significant improvement over the previous eight runs but which still falls short of the goal (12 kOe). EBSD analysis shows about 41.3% of the grain is aligned. Based on our experience with stir friction welding of ferric steel plates, we believe the texture can be further improved to >80%. Consequently, we believe we can push the coercivity to benchmark.

The key achievement for this project in FY 2012 is that we demonstrated textured nanostructure using friction consolidation method. Though still needing significant optimization, the method is proven, holding all key characteristics required to fabricate next generation nanocomposite magnet. Based on these findings and together with Ames and the EEC, we proposed a technology demonstration program to Advanced Research Projects Agency-Energy. Moreover, we proposed an independent task in the critical materials hub proposal for developing the friction consolidation method.

Our final goal is to establish PNNL as the leader in the field of nanocomposite fabrication. Our target applications include permanent magnet, soft magnet, and structural materials.

PN11064/2386

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

Dongsheng Li

This project is developing* 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 the environment are key issues challenging mankind and are central to DOE's mission. Many fundamental scientific problems related to energy and environmental issues involve control of chemical and biological processes. Advancement in scientific innovations is often controlled by precise, atomic-level characterization of materials of interest as this, in turn, renders the ability to control/manipulate material properties. However, existing tools and capabilities to measure molecular details of chemical and biological reactive site structure and function limit our understanding and ability to control natural- and human-made systems. To understand energy/environment materials is to capture and visualize atomic-level mechanisms under dynamic operating conditions, such as the structural evolution of active materials in a battery during its operation, a catalytic process during system function. Though structural and spectroscopic information under high vacuum conditions have been developed to a level that can typically be used routinely (such as aberration-corrected scanning/transmission electron microscopy [S/TEM], atom probe tomography [APT], and scanning probe microscopy [SPM]), 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 atomic-level imaging and spectroscopic analysis of energy and environment materials under *in situ*/operando condition and create much-needed materials for next generation energy and environment applications. This will be achieved by extending the state-of-the-art aberration-corrected S/TEM and other microscopy and imaging capabilities to a new level, enabling atomic-resolution imaging and spectroscopic analysis under dynamic operating conditions. New capabilities will be developed to support complementary integration of site-specific atomic resolution structural and chemical information obtained from various techniques, including S/TEM, APT, and focused ion beam and scanning electron microscopy (FIB/SEM).

During FY 2012, we made several key accomplishments for advancing chemical imaging capabilities in PNNL. We used these capabilities to probe the fundamental scientific challenges of energy and the environment. Our work was carried out from three aspects: energy storage materials, catalysis, and integration of capabilities across the platform of S/TEM and APT. First, continuing our previous S/TEM effort, we developed the capability of electron energy loss spectroscopy (EELS) over the last year that enables the probing of chemical identity, electronic structure, and the coordinate chemical environment around a specific atom with high spatial resolution. The EELS and STEM imaging offer the opportunity to study energy-related materials at the atomic level with 0.3eV energy resolution. Additionally, we established a new capability, aberration corrected environmental TEM (ETEM), which provides an Angstrom level resolution under oxidizing/reducing gases environment with pressure to 20 mbar and temperature to 1200°C. This unique capability enables observation of the chemical process under realistic conditions, such as imaging of catalytic materials under a gaseous environment at high temperature.

We a developed wet electrochemical cell that can be used in two modes: plain liquid cell (allows imaging of liquid sample) and biasing liquid cell (enables biasing of sample under liquid environment). The wet electrochemical cell extends our imaging capability to allow probing into phenomenon such as nanoparticle nucleation and growth in liquid, solid-liquid interface, and the electrochemical dynamic process. Essentially, this capability will provide us a unique opportunity for probing into challenges facing the lithium ion battery community, which include determining why lithium batteries fail following cyclic charging and discharging.

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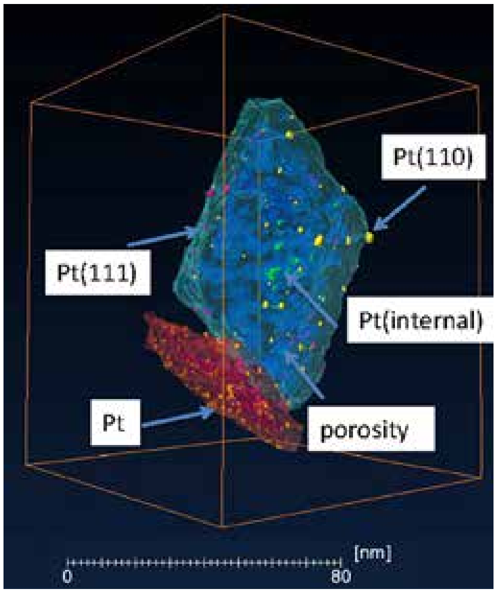
We also developed an inert gas environment for handling of air-sensitive samples. This capability allows us to handle lithium metal, an essential component for lithium ion, air, and sulfur battery research. The fundamental *in situ* concept and capabilities developed in this project have a significant impact on the research community for energy materials. Our *in situ* concept has been implanted and used by other national laboratories and universities across the globe, the result of which advances the field of *in situ* studies of energy materials. At the same time, we enhanced the capability that enables imaging of a sample across the platform of FIB, APT, and S/TEM, which are key for imaging a specified site of a sample across different instrument platform and yield complementary information. These new capabilities enable probing energy materials under reaction conditions and capturing complementary information across different instrument platforms.

With these new capabilities, we probed into the following scientific questions. For energy storage direction, we studied the energy storage characteristics of silicon. In theory, silicon has a storage capacity of ~ 15 times of graphite, which is currently used in rechargeable batteries for electronic devices. However, when inserting lithium into silicon, the latter will expand ~ 300%, which will cause the short battery life cycle. Using our *in situ* TEM capability, we studied the lithiation behavior of silicon/silicon and carbon nanocomposite. These studies led to three high profile journal publications, which provide essential information for tailoring new materials based on silicon and carbon to allow high capacity, long cycle life, and the safe operation of the lithium ion battery. We also initiated collaborating research activities with leading industries such as GM and Applied Sciences to understand the fundamental properties of materials they are developing for electric vehicle batteries.



Tomography and high-resolution study of γ-Al$_2$O$_3$ surface structure and Pt surface interaction. The reconstruction of *g*-Al$_2$O$_3$ is decorated with Pt.

For catalytic materials, we used the newly established *ex situ* and *in situ* to study fundamental issues of phase transformation, surface structure, and metal-surface interaction for a γ-Al$_2$O$_3$ heterogeneous catalyst system. To perform this study, we developed and synthesized a morphologically well-defined γ-Al$_2$O$_3$ catalytic support that represents a model system but is highly representative of industrially relevant, high surface area γ-Al$_2$O$_3$. Atomic-level TEM studied has revealed for the first time a detailed reconstruction of the surface structures of transition Al$_2$O$_3$ surfaces. The S/TEM high-resolution observations under in situ heating conditions have been applied to study the atomic nature of coalescence, revealing the coarsening mechanism of the Pt nanoparticles supported by γ-Al$_2$O$_3$.

For the integration of STEM, FIB/SEM, and APT, we studied the system of Au nano-clusters embedded in MgO and performed high resolution STEM imaging and APT analysis on similar tips. Highly coherent, sharp interfaces were observed between Au-nanoparticle and MgO. We found that the nanoparticles are composed of Au, Mg, and O, as evidenced by the APT data. This work provides the fundamental data for identifying the laser-induced atom evaporation in the APT. The work has been published in *Nanotechnology*.

Throughout FY 2012, our work in this project has led to seven peer reviewed journal publications, three invited talks, and 15 conference presentations. We are the leading organizer for a symposium titled "Frontier of Chemical Imaging across the Electrons, Photons, and Ions" for the MRS 2012 Fall Meeting in Boston, and we organized a PNNL seminar and workshop. In addition to a *Microscopy Today* 2012 Innovation Award, we applied to a DOE proposal and are subcontracted for 3 years with Argonne National Laboratory (ANL) for that battery project.

Looking toward FY 2013, we will focus on establishing *in situ* imaging methods and procedures to study the stability of catalytic nanoparticles under oxidizing and recuing conditions. We are also attempting to develop discrete tomography capability for imaging of catalytic clusters under *in situ* and *ex situ* conditions and are in the process of integrating current TEM imaging with x-ray spectroscopy experiments (performed at ANL) and *ab initio* modeling toward developing a physical-based understanding of catalytic phenomena.

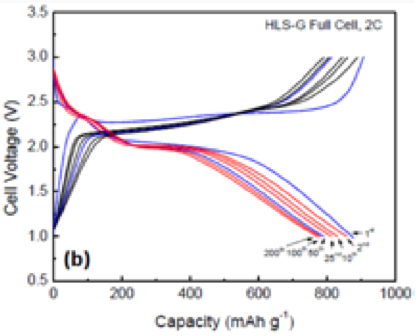
Three-Dimensional Structured Composite Nanomaterials for Energy Storage

Xiaolin Li

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 3D structured composite nanomaterials will bring revolution to electrode materials and structures and assist with the advancement of lithium batteries.

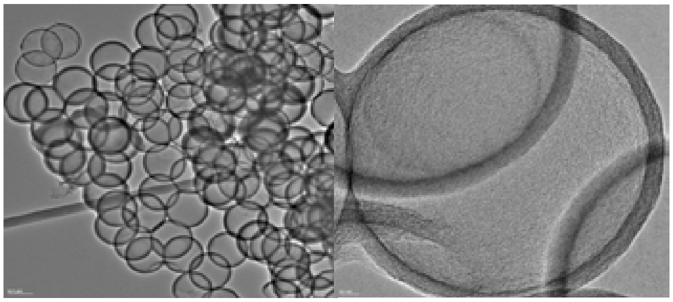
The lithium sulfur (Li-S) battery is a promising technology with high theoretical specific capacity. Unfortunately, it suffers from extremely poor stability due to the dissolution and shuttle effect of polysulfide anions during charge/discharge cycles. Three-dimensional structured composite nanomaterials will integrate electroactive material (sulfur) and mechanically stable conductive framework to provide good electrical and mechanical integrity. These conditions also void space to provide diffusion channels for the electrolyte. It is thus important to develop 3D structured composite nanomaterials for Li-S batteries.

Our project is developing economic synthesis, assembly, and integration approaches that enable cost-effective production of desirable 3D applications and fundamental understanding of the roles of each nanomaterial component and their interfacial interactions. PNNL has made a significant investment in energy storage and has developed strong programs in Li-ion batteries, Na-beta batteries, and redox flow batteries. This Li-S investment is critical for energy storage technologies beyond batteries and for breakthrough concepts in inexpensive, large-scale energy storage.



Charge-discharge curve of Li-S battery with mesoporous carbon-composite (22 nm, 50% sulfur loading) as cathode and graphite-Li hybrid anode.

In FY 2010, we synthesized a structured graphene-sulfur nanocomposite as cathode materials for the Li-S battery. Coated with a thin layer of cation exchange film, the shuttle of polysulfide anion from the 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. For FY 2011, we synthesized a series of mesoporous carbon (MC) materials with tunable pore sizes and pore volume, systematically investigating their application as a conducting matrix to incorporate sulfur into the Li-S batteries. An initial capacity of ~1100 mAh/g and retention of ~600 mAh/g over 50 cycles were obtained. We found that partial sulfur filling and surface modification led to improved battery performance by promoting the electrical contact between sulfur and MC, thereby reducing dissolution/diffusion of polysulfide anions and producing a steady supply of lithium ions.



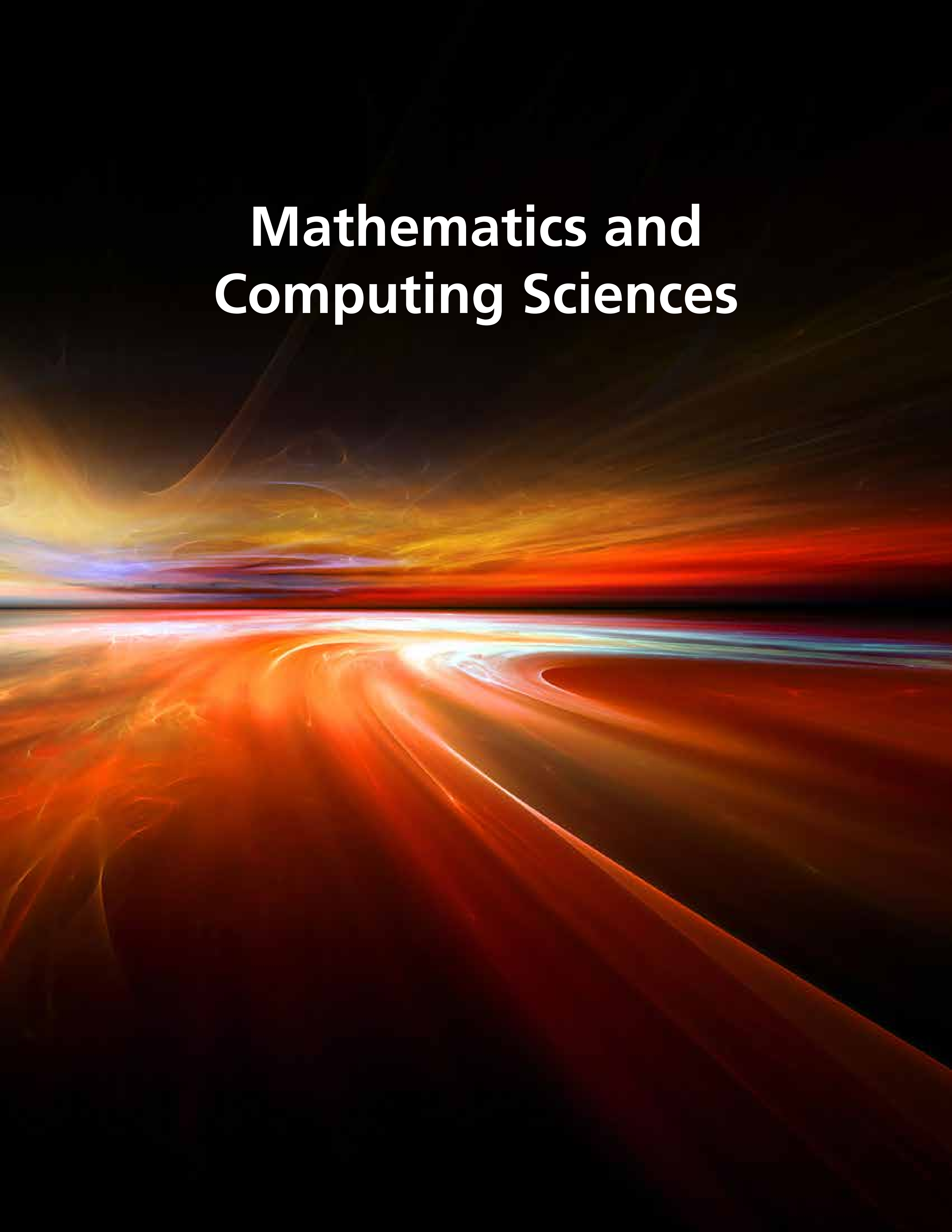
TEM image of hollow carbon spheres with ~300 nm diameter.

In FY 2012, we applied the mesoporous carbon-composite (22 nm, 50% sulfur loading) as cathode and graphite-Li hybrid anode for Li-S batteries. With the new anode design and good confinement effect at the cathode side, the shuttle effect of sulfur was alleviated. The materials produced good cycling stability with the capacity of ~800 mAh/g for over 300 cycles. In another approach, we synthesized hollow carbon spheres with tunable pore size of 300 nm or 100 nm using the hard template method. These carbon spheres have high conductivity because of the conjugated carbon precursor. The large void space in the middle of the hollow carbon spheres will greatly increase the sulfur loading. As mesopores at the carbon wall provide electrolyte diffusion channels, this unique structure helps confine the polysulfide anions inside the hollow sphere and alleviate the shuttle effect.

We also built an electrospin equipment to synthesize pure or composite carbon fibers for Li-S battery cathodes. The diameter and porosity of these fibers can be controlled by adjusting the concentration of the polymer precursor and adding pore-generation reagents. The carbon fibers of hollow carbon nanospheres have been synthesized using the electrospin method. They can be used not only as new cathode materials for Li-S batteries but also as cargo for fundamental study such as *in situ* characterizations.

PN10074/2316

Mathematics and Computing Sciences



A Distributed Systems Architecture for the Power Grid

Jenny Yan Liu

This project demonstrates the efficiency of a distributed system architecture for decentralizing power models in a large-scale power grid. The architecture eliminates the bottleneck of a centralized location for overloaded data management, monolithic computation, which is increasingly a burden to fast-growing data rates and quantity.

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. Fast distributed monitoring and analysis applications are increasingly important to power system operation and control. A distributed systems architecture testbed for evaluating power system distributed applications is critical to plan the deployment of HPC platforms to connect their decentralized electric power applications and form the guideline of distributing power applications to meet real-time requirements of critical operations and control in the electric power system.

Our previous implementation has the peer-to-peer data exchange through TCP sockets. Therefore, the data communication logic has been hard-coded in the power application. This mechanism has limitations for validating distributed power models (such as the state estimation algorithm), as the study of algorithm behavior requires that different partitions of the same power grid network be tested. The partition may change how the sub-areas are connected, hence peer-to-peer interactions. Hardcoding the data communication in the state estimation code is not sufficiently flexible to represent the procedural steps of the distributed state estimation.

Our research project further enhances the distributed systems architecture we developed in FY 2012 and introduces a service-oriented layer that contains a workflow environment for composing distributed procedural steps, observing data exchanges individually, automatically launching remote jobs running on HPCs. This layer also links to the coordination and fault-tolerant middleware, as coordination logic is developed in the middleware. The architecture is implemented as a middleware platform that coordinates distributed procedural behavior and adapts to runtime computing conditions to improve reliability, maintain causality, and guarantee responsiveness. The middleware is equipped with a modeling tool to estimate how the distributed power model is affected by factors of data communication, geographical locations, and computing resource demands. As a result, this research facilitates the design of cost-effective situational awareness applications within a large-scale power grid.

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 from FY 2012 is a software demonstration deployed on the PowerNet Lab testbed that encompasses:

- scalable middleware that, beyond connecting distributed code, coordinates the dynamic data communication according to various synchronization criteria
- an orchestration framework that monitors a step-by-step data exchange
- a prototype of distributed state estimation with PMU data
- a testbed environment leveraging the laboratory
- rigorous simulation/analysis tool on end-to-end delay estimation.

In addition, the architecture demonstrated the ability to provide open interfaces with plug-and-play power system applications to a data communication platform, offered support to connect distributed applications in any language and protocols, and provided optimized solutions for deploying distributed power applications on available HPC clusters given resources and real-time latency constrains.

In FY 2013, we will integrate this distributed systems architecture with other power grid applications and infrastructures. We are targeting integration efforts, including developing PMU failure detection using Volttron™ platform, which has the capability to designate agents to substations and launch the agents to collect PMUs working status. Integrating our architecture with Volttron™ agents, allows the middleware to investigate whether a PMU is working in the normal state. In addition, we will integrate with GridOPTICS™, a plug-and-play platform to bridge various power applications to data storage, management and access. The PMU data access in distributed state estimation is one application to be supported by GridOPTICS™, and the architecture will communicate with GridOPTICS™ API. The success of this integration will lead to quick deployment of distributed systems to support power grid applications. The solution enables this and similar projects to make informed choices when balancing real-time delays and resource capacities.

PN11002/2324

A Multi-Modal Integration Framework for Chemical Imaging

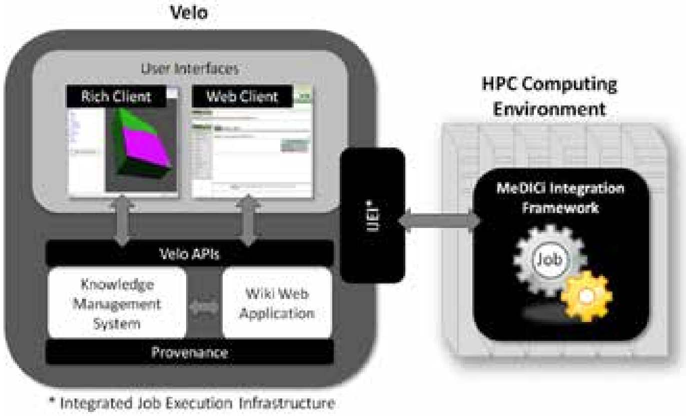
Kerstin Kleese van Dam

This project will deliver an open multi-modal integration framework for chemical imaging to allow the fast and precise analysis, comparison, and integration of experimental results from several imaging technologies against the background of exponentially growing data volumes, acquisition rates, and data complexity and an increasing need for real-time analysis.

PNNL aims to further imaging informatics by developing real-time analysis capabilities across different chemical imaging technologies, supporting improved scientific results through more complete information during the experiment. Our focus is to define the correct capabilities and optimal implementation to facilitate integration within a highly distributed, high data rate environment. The proposed framework for chemical image analysis and integration therefore necessarily includes capabilities for data preservation, descriptors, management, and analysis. There is currently no suitable framework available or under development worldwide that appropriately handles the multitude of chemical imaging results and provides scalability to petabytes of data. Initial steps at a number of facilities to install single experiment pipelines can automatically capture and analyze results; at the forefront, for example, is the crystallography community. The new framework will bring together a range of existing research concepts in semantic mapping and rules, workflows, and core technologies for the capture, analysis and integration of experimental data, integrate and develop these further to create this unique capability. In addition to achieving desired goals, the technology underlying this framework will potentially have a range of applications beyond chemical imaging.

The PNNL framework is being developed to support multi-modal imaging with particular emphasis on real-time analysis to allow experimental steering and correlation of results across different modalities. In its core exemplary components, the project is building on existing efforts such as developing capabilities for data acquisition, annotation, and storage (ICAT and MeDICi), collaborative data management and analysis, semantic characterization, data compression, data reduction, image reconstruction, segmentation, registration, and visualization. In this project, we aim not only to extend existing capabilities to support real-time image analysis, but we are also looking to identify core analysis capabilities essential to larger groups of analysis workflows, thus moving toward more sophisticated analysis methods. Further, we are exploring the potential for the guidance and automation of the analysis processes with single instruments and, more importantly, across imaging modalities. The proposed environment consists of a highly customizable collaborative data management and analysis infrastructure (Velo) and Rapid Experimental Analysis (REXAN) framework that provide reusable components for data management, annotation, compression, reduction, reconstruction, registration, and segmentation to the community, and offers the opportunity to integrate community developed capabilities into the framework.

Velo is a reusable, domain independent, eScience environment, and knowledge management infrastructure for modeling and simulation. Velo leverages, integrates, and extends Web-based open source collaborative and data management technologies to create a scalable core platform that can be tailored to specific science domains. Velo helps scientists to organize experiments, computations, and large and complex datasets used in scientific modeling. It is currently deployed in domains as diverse as carbon sequestration, climate modeling, chemical imaging, and environmental remediation.

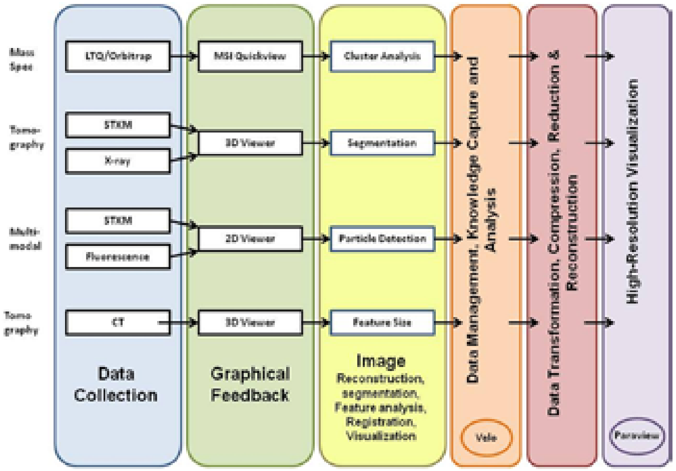


Chemical imaging architecture combines the MeDICi Integration Framework and Velo infrastructure.

As shown, Velo gives scientists two different interfaces for interacting with data: a lightweight Web-based interface and a full-featured desktop client. The interfaces allow scientists to manage their research from within the context of their projects without having to manually find/invoke tools and manipulate data. The collaborative nature of the user interfaces also allows scientists to work together and share research with others. Science domain-specific tools can also be simply plugged into Velo and exposed to users through the Web or desktop tools. Velo includes integrated Wiki capabilities so that objects like simulations and input files can automatically be annotated by users through familiar wiki editors. The Wiki components additionally provide semantic markup, search, and query capabilities that can be exploited to support a wide range of knowledge management and collaboration requirements.

Velo leverages a mature, graph-based knowledge management system, Alfresco, as its foundation. It provides data storage and a rules framework as well as key functionalities such as versioning, metadata management, and relationships between datasets, projects, and tools (models, scripts, applications, workflows). The CII architecture also integrates Velo with the MeDICi workflow engine for running complex pipelines to process and transform instrument data into visualizable datasets. MeDICi is a middleware platform to integrate data- and compute-intensive processing components with data sources and visualization tools across multiple scientific domains. MeDICi is connected to Velo through the use of Velo's Integrated Job Execution Framework (IJEF), which seamlessly connects MeDICi running on an HPC server to the knowledge management server and user interface. It automatically stages all required input files, submits the MeDICi workflow job, monitors the running workflow (updating status information in real time), and performs simulation-specific post-processing operations such as filtering results or streaming results (or remote links to large data sets) back to the knowledge management system for integration with analysis tools.

We contend that it is possible to describe most analytical pipelines through a limited set of conceptual workflows that have a range of recurring components that can be reused across a range of conceptual workflows. Therefore, a set of libraries containing highly optimized versions of those reusable components would help with the accelerated development of new analytical pipelines as well as raise the overall speed, scalability and performance of the resulting pipelines. In FY 2011, the project identified the core components for such analytical pipelines in collaboration with the initiative researchers and stakeholders and



REXAN framework and its mapping to specific use cases.

began developing two test analysis capabilities. In FY 2012, we analyzed the results of our initial analytical tools and created a framework set of libraries of reusable components for the flexible creation of analytical pipelines for both single and multi-modal experiments. The integrated Velo/REXAN system was then used to create a range of analytical pipelines and tools now used in production by the scientists:

- PNNL High Resolution Mass Spectrometry – reduces analysis times from hours to seconds and enables much larger data samples (100 KB to 40 GB) at the same time
- ALS X-Ray tomography – reduces analysis times of combined STXM and EM data collected at the ALS from weeks to minutes, decreases manual work, and increases data volumes to be analyzed in a single step
- Multi-modal nano-scale STXM and TEM data analysis – provides a semi-automated process for particle detection.

In FY 2013, we will productize the analytical environment for distribution to other partners, continue to expand its functionality and utilize the framework to develop more analytical pipelines.

A Scalable Fault Tolerance Infrastructure and Algorithms with Programming Models and Scientific Applications

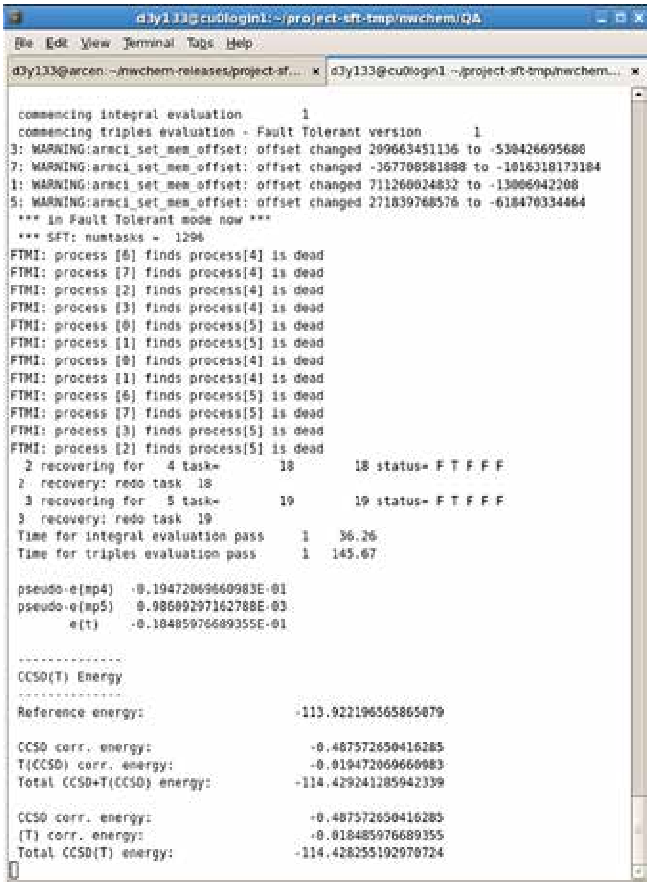
Abhinav Vishnu

Delivering fault tolerance on exascale computing platforms with millions of processing elements and components will enable leading-edge scientific applications to utilize the performance of these systems to accomplish scientific discovery and innovation to 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 remaining major 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 that embodies several components required to provide fault tolerance to the applications. These components include scalable fault detection using hardware mechanisms provided by the modern systems, low overhead mechanisms of propagating this information to useful entities in the system to reduce overall recovery cost, and leveraging the infrastructure for hard 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), a high performance communication runtime system. The infrastructure is also being used by programming model layers such as Global Arrays. Our objective is also to develop high performance and fault tolerant computational chemistry methods such as the coupled cluster method 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 that 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.

In FY 2010, we developed initial fault tolerance management infrastructure, providing 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 communication infrastructure was presented at the 2010 International Conference on High Performance Computing. Specifically 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 laboratory during this period.



```
 commencing integral evaluation        1
 commencing triples evaluation - Fault Tolerant version       1
3: WARNING:armci_set_mem_offset: offset changed 209663451136 to -530426695680
7: WARNING:armci_set_mem_offset: offset changed -367708581888 to -1016318173184
1: WARNING:armci_set_mem_offset: offset changed 711260024832 to -13006942208
5: WARNING:armci_set_mem_offset: offset changed 271839768576 to -618470334464
 *** in Fault Tolerant mode now ***
 *** SFT: numtasks =  1296
FTMI: process [6] finds process[4] is dead
FTMI: process [7] finds process[4] is dead
FTMI: process [2] finds process[4] is dead
FTMI: process [3] finds process[4] is dead
FTMI: process [0] finds process[5] is dead
FTMI: process [1] finds process[5] is dead
FTMI: process [0] finds process[4] is dead
FTMI: process [1] finds process[4] is dead
FTMI: process [6] finds process[5] is dead
FTMI: process [7] finds process[5] is dead
FTMI: process [3] finds process[5] is dead
FTMI: process [2] finds process[5] is dead
  2 recovering for    4 task=        18        18 status= F T F F F
 2  recovery: redo task  18
  3 recovering for    5 task=        19        19 status= F T F F F
 3  recovery: redo task  19
 Time for integral evaluation pass     1    36.26
 Time for triples evaluation pass      1   145.67

 pseudo-e(mp4)  -0.19472069660983E-01
 pseudo-e(mp5)   0.98609297162788E-03
        e(t)    -0.18485976689355E-01

 --------------
 CCSD(T) Energy
 --------------
 Reference energy:                    -113.922196565865079

 CCSD corr. energy:                     -0.487572650416285
 T(CCSD) corr. energy:                  -0.019472069660983
 Total CCSD+T(CCSD) energy:           -114.429241285942339

 CCSD corr. energy:                     -0.487572650416285
 (T) corr. energy:                      -0.018485976689355
 Total CCSD(T) energy:                -114.428255192970724
```

The output of a run on eight processors across four nodes, demonstrating the successful recovery from a single-node failure.

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 Conference is a premier conference that attracts 9000+ attendees from across the world. Cray Seastar is a proprietary network used on the Oak Ridge National Laboratory Jaguar supercomputer system. There were many attributes to the design and development of infrastructure, with our design able 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 actual cost of recovery to be proportional to the degree of failure. To meet this stringent requirement, we designed and developed an adaptive method for fault detection to leverage hardware mechanisms as much as possible while using software timeouts when the hardware mechanisms cease to exist. To expedite recovery cost, we designed fault tolerant collective communication primitives to broadcast the information efficiently with minimal performance degradation. A combination of these capabilities ensured that the cost of recovery was proportional to the degree of failure.

A critical component of the infrastructure is the fault tolerant process manager. In the previous year, we designed one for InfiniBand based systems, but 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 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 with the state-of-the-art checkpoint/restart systems that allow 85% of CPU cycles to be available for computation, our proposed solution outperforms them by a significant margin.

Most of the research proposed above considers hard faults, those in which components become permanently unresponsive. While these failures are increasingly prevalent, there is another class that 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 could have high accuracy with minimal data replication and recomputation on the fly. We designed an approach for Density Functional Theory in computational chemistry focusing on different attributes of data in the computation. We believe that our 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 made significant strides in designing and developing fault tolerant solutions for computational chemistry and global arrays, specially looking at soft errors. We first completed the remaining non-fault tolerant elements in computational chemistry, especially singles and doubles that are iterative in nature but require much more intricate understanding of the algorithm for fault tolerance. However, the primary focus in FY 2012 was soft errors, especially due to growing concerns of these types of errors in upcoming large-scale systems.

We performed an in-depth analysis of computational chemistry routine sensitivity to bit flips. The undertaken approach is statistical for an insight on the effects. We executed a large number of simulation runs with bit-flips in many important data structures to understand flip sensitivity, with the results divided into four quadrants: 1) the simulation took same number of iterations and the result was correct; 2) the simulation took larger number of iterations and the result was correct; 3) the simulation converged with incorrect results; 4) hang/abort due to mishandled exception. About 46% fell in the first category, implying that many of the bit flips can be handled successfully in iterative procedures without a need for extra fault tolerance strategy. Approximately 13% required extra iterations, which leaves us with 41% of the runs that resulted in failure. We are currently using this study to define numerical assertions that can allow the handling of 80–90% of failures. We expect that it would be difficult to handle 100%; however, we can handle a significantly higher number of failures with simple, effective numerical assertions.

Actionable Visualization Tools For Power Grid Situation Awareness

Luke Gosink

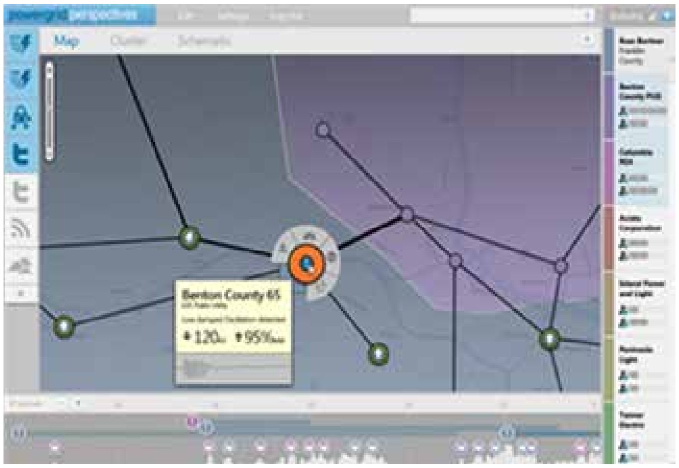
A sustainable, efficient power grid operation relies heavily upon real-time information transparency and wide-area situation awareness (SA) for all organizations in the grid. This project addresses the fundamental need for greater SA within the grid domain through the design of actionable visualization strategies that increase inter-organizational communication and collaboration.

Without real-time, system-wide awareness in the power grid, there is significant potential for small local power instabilities to escalate and cascade into large-scale blackout events. While many organizations have developed methods that support internal SA capabilities (i.e., awareness of state within the organization), there is little evidence of successful research that can help organizations to see across organizational seams in order to increase external SA. In this context, there is need for new visualization methods that can better support external SA needs by broadening the conduit of communication between organizations to support wide-area, high-level monitoring and collaborative problem-solving efforts.

This project will support the need for external SA by designing a new visual communication mechanism that will allow organizations to share information securely across organizational boundaries. We will extend this mechanism with new visual analytic strategies that incorporate information outside of the power domain (e.g., weather, political/social, cyber, etc.) so that organizations have a better awareness of events that can potentially impact grid stability. We will support access to these functionalities through a new application, Shared Perspectives, that will allow power system operators to achieve broader a SA of events both within and outside of the power grid.

Project progress is based on two fundamental objectives: creation of a master specification document for fostering SA that identifies use-cases, challenges, and needs of operators when they attempt to share information during critical events; and the design and implementation of the Shared Perspectives visualization application that directly addresses challenges identified within the master specification document.

During FY 2012, significant progress was made in compiling the master specification document. We conducted numerous interviews with organizations (including representative cases of utilities, balancing authorities, and reliability coordinators) to identify the need for external SA. Additionally, we attended several workshops and seminars to identify current approaches used to generate this awareness.



Shared Perspectives application.

Based on our initial research, we identified that organizations are lacking in methods that support external SA. Operators communicating across organizations often depend exclusively on telephones to create a foundation of common understanding. For non-critical situations, this communication medium is sufficient; however, growing evidence indicates that during critical, complex events, relying on phone communication alone creates significant opportunity for miscommunication that can result in disastrous consequences. To address this challenge, our research identifies the need to broaden the communication conduit through a common tool that supports both audio and a common visualization perspective where organizations can "push" and share various types of information to help build common understanding.

From our findings, we initiated design work for the Shared Perspectives application that addresses the need to flexibly and securely build common understanding between organizations through information sharing. A prototype for this tool has been constructed and is currently being used to initiate conversation and feedback from industry. The tool itself is based on a scalable web architecture that supports a highly interactive collection of visualization components. This set of components enables the rapid design of custom applications for industry use-cases.

In FY 2013, we will continue industry engagement to further our research on the master specification document. Toward this task, we will begin to demonstrate the application on larger use-cases and solicit a broader range of industry feedback. A final task for FY 2013 will be to design and perform a validation study on the effectiveness of Shared Perspectives to reduce time-to-resolution for various events.

PN12003/2404

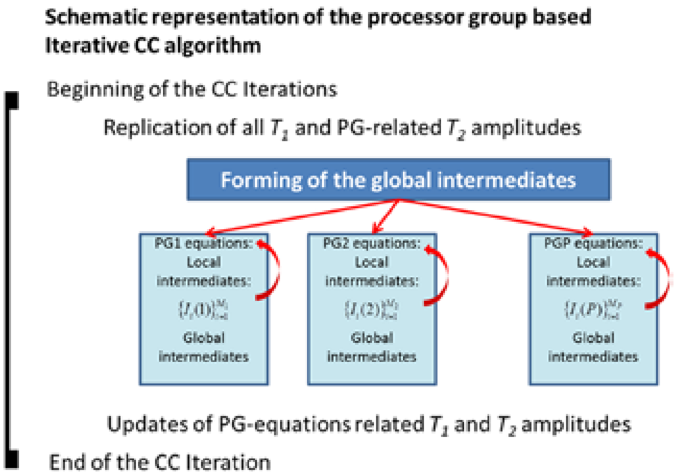
Advanced Optimizations for Extreme-Scale Homogeneous Systems

Darren Kerbyson

In this project, we combine techniques aimed at tackling performance, power, and reliability on the latest supercomputers that contain a massive number of homogeneous processor cores.

Computing at extreme scales increasingly requires the combination of advanced techniques to achieve reliable, high performance at acceptable energy efficiencies. It is critical that all components are considered in combination on future supercomputers in the context of applications of interest to obtain high computational rates and achieve the most science on the available systems. PNNL has enabled the exploration and development of techniques for enabling performance analysis, fault tolerance, energy efficiencies, and optimizations for advanced computational resources, including GPUs and multi-core processing nodes. For this project, we aim to go one step further and explore the use of these techniques in combination, as appropriate, in the context of the largest systems. In particular, we target systems that comprise homogeneous processor-cores.

This project focuses on the development and integration of capabilities in performance diagnostics, energy efficiency optimizations and software fault tolerant techniques with a particular emphasis on data movement. The work will be applied to molecular science applications and targets systems such as Cray XE6 and Cascade type systems as well as IBM Blue Gene/Q systems. Our specific aims are to 1) develop performance diagnostics applicable to Global Arrays applications that allow both detailed and summary profiles to assist in bottleneck identification; 2) integrate the novel Energy Template approach for optimizing energy use into the PNNL Molecular Dynamics application code; 3) explore optimized Global Array implementations on the latest advanced homogeneous systems; and 4) develop data-centric approaches optimizations that can be applied to PNNL's coupled cluster (CC) molecular science applications.



Processor groups localize data required in the computation of a coupled-cluster (singles, doubles) CCSD calculation. Each subset uses local replication of input data, reducing communication across a large-scale system.

With a mid-year start, our work on performance diagnostics centered on the use and extension of the HPC toolkit to analyze applications that use the Global Arrays toolkit. Currently, there are no available tools that attribute performance information to global data objects, but there is a need to understanding data motion not only for performance but also for energy consumption. We enabled HPC toolkit to examine global data object with respect to time, rank, and calling context. Use performance included metrics such as "bytes accessed per non-local read" and "average latency per blocking write." To collect profiles and traces at scale with minimal overhead, we combined the sampling of remote reads and writes with that of program behavior in the calling context. The analysis of the PNNL Molecular Dynamics ARGOS application was demonstrated and enables an analysis of its use of GA, in particular the code and amount of global data transferred. These findings were presented at the Workshop on High Performance Infrastructure for Scalable Tools (WHIST '12).

The latest in the Blue Gene BG/Q was to explore and optimize Global Arrays for its use at extreme scales. Notably, BG/Q was at both Lawrence Livermore National Laboratory and Argonne National Laboratory this year in systems that have achieved unprecedented levels of performance and concurrency. Our work has enabled Global Arrays to maximize low-level communication primitives available on BG/Q and has overcome some architecture limitations, including the absence of atomic memory operations (AMOs). An in-depth performance evaluation of its implementation has been undertaken, which demonstrates its use in medium-scale (up to 4,096 processor-cores) runs of NWChem's SCF operation. A report on this work is being prepared for publication.

The general structure of the processor-group-based iterative CCSD (CC with singles and doubles) algorithm has been developed and implemented. This has been achieved

PN12006/2407

through the partitioning into subsets the whole set of the CCSD equations where each subset is characterized by singly and doubly configurations or by corresponding spinorbital indices. Each subset is formed on a corresponding processor group (PG), and has enabled us to effectively localize the data needed for each subset reducing the communication requirements across a system. Our current algorithm enables the user to exploit an arbitrary number of processor groups.

For FY 2013, we will incorporate an energy template into ARGOS that will use energy saving techniques on a per processor-core basis when cores have significant wait times.

We will also extend our data centric analysis of applications within the HPC toolkit aimed at costing data movement and will use CCSD to quantify effectiveness of the processor-group version that localizes its global data accesses. In addition, we will extend testing of the CCSD PG version on algorithms where the relevant subset of two-electron integrals and doubly excited cluster amplitudes will be copied to a corresponding PG. This new algorithm will be fully integrated with the new four-index transformation for the unrestricted Hartree-Fock case.

Advanced Statistical Network Models for the Integration of Experimental and Open Source Textual Data for Bioforensic Analyses

Bobbie-Jo M. Webb-Robertson

This project is developing a statistical methodology from composite signatures to identify possible 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 extracting 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.

This project developed a computational framework to quantify statistically entity identification (person, place, etc.) associated with biological sample origin through applying composite signatures. The first set of data includes traditional experimental forensic approaches, such as chemical composition to determine culture media, genomic information, and proteomic data. The second set is analytical about capabilities required to grow the sample and includes results of scientific literature and a list of scientists and other personnel associated with those publications.

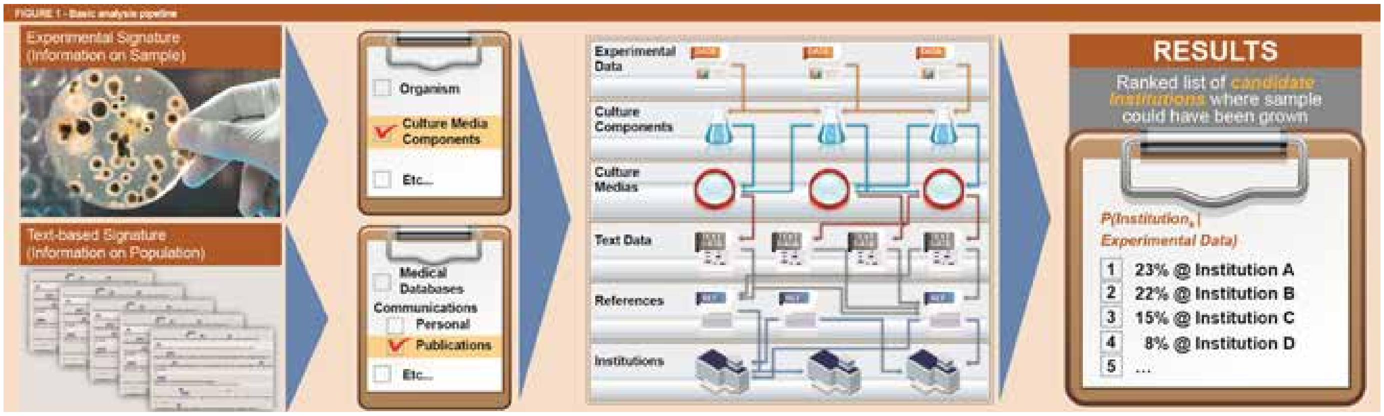
In FY 2011, our work led to two major development creations, which are described below.

Complex Biomedical Event Extraction Pipeline. 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. The developed pipeline was leveraged to search scientific publications for specific types of culture media. The event extraction pipeline was used to generate signatures of each publication in our open-source dataset in simple binary vectors based key terms.

Methodology for composite signature generation. Composite signature generation was derived in a Bayesian framework. The conditional independence of data streams allowed information integration directly to a final probability of interest: institution *(I)* given the experimental evidence and $P(I|ED)$. The network linked experimental and textual data through a culture media node. The textual signature developed from the event extraction pipeline was used to define the appropriate conditional probabilities.

For FY 2012, we generated the full composite Bayesian network and tested it on an annotated set of documents and data for *Bacillus anthracis* and *Yersinia pestis*. We illustrate that the Bayesian network model can assign a higher posterior probability than expected by random chance to appropriate institutions when trained using only a small set of manually analyzed documents.

The results of this project demonstrate that it is both feasible and advantageous to integrate laboratory measurements with automated text searches in a probabilistic manner for investigative microbial forensics.



The basic framework of Bayesian composite signature generation for the purpose of bioforensic attribution.

Compressive Sensing for Threat Detection

Luke Gosink

This research improves 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 threats in a noisy environment or during instances when they are purposefully obscured.

Compressive sensing is class of algorithms that provides methods for reconstructing observations or measurements from data streams that are incomplete, degraded, or obfuscated when the data meet certain mathematical conditions. While compressive sensing is a highly active research area and has provided some 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:

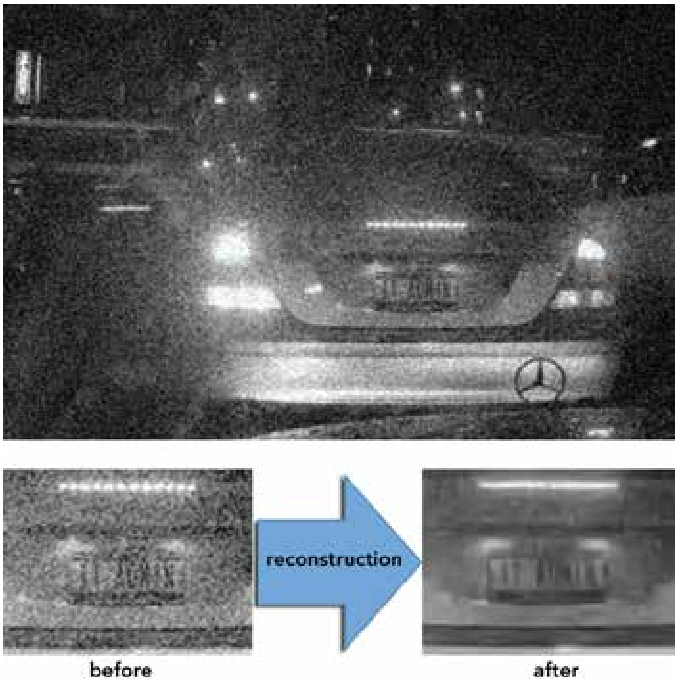
- Detecting signatures from a degraded data set, such as in the presence of noise, interference, or obfuscation. The degraded measurement is reconstructed using compressive sensing, and we determine if the needed features are identifiable in the reconstructed data so that the threat signature can still be detected.
- Detecting signatures in time- and data-constrained environments. Efficiency can be increased by allowing the sensor either to capture or transmit less data than in normal operation. We will quantify the level to which we can lower the data acquisition or data transmission rate and still detect the signature.

A successful outcome of this work will provide an improvement in the robustness of signatures as well as increased efficiency of data capture for signature detection. Additionally, our work will provide knowledge of how efficiently noise and interference can be mitigated in an operational scenario and how best to allocate specific 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 created and evaluated a large number of test cases to determine the optimal parameter configuration to use for the compressive sensing algorithm that would optimize signature detection performance. During FY 2012, we augmented these capabilities of our software tool by supplying additional algorithm capabilities to improve signature detection performance and increased the speed at which a signature detection could be performed. We also adapted our tools to run in a high performance computing environment and integrated them into a specific analytical framework to allow their use in conjunction with other analysis capabilities developed by the initiative.

We have applied and experimented with our methods using a variety of observational data types including multiple types of image and spectral data. Our primary FY 2012 target data set was an infrared spectroscopy (IR) sensor designed to detect signatures of airborne chemical threats. In an initial proof-of-concept study, the use of our tools improved sensor performance by significantly decreasing the number of false positives caused by unknown interferent chemicals.

Our research plan for FY 2013 is designed to guide the project to its successful completion and has two pieces. First, we will improve the usability of our software tool by adding an intelligent search algorithm to reduce the number of test cases needed to find the optimal parameter configuration to use to apply compressive sensing to a particular data problem. Second, we will complete an analysis of the IR data set, expanding the problem to look at multiple threat chemicals combined with multiple interferent chemicals.



The use of compressive sensing to reconstruct a noisy image so that the features of interest representing the signature (i.e., the digits of the car’s license plate) are enhanced and more readable.

PN11013/2335

Computational Optimization and Predictive Simulation for Synthetic Biology

Bill Cannon

We are developing a multi-scale predictive simulation capability for biology similar in spirit to multi-physics codes based on physical principles that will couple metabolic reactions of microorganism with their environment and allow for dynamic optimization of metabolic processes to the available nutrients and environment.

The goal of this project is to develop a multi-scale predictive simulation capability for biology that is predictive and reliable. Currently, flux-based simulation approaches are the method of choice for modeling metabolism because they do not require the use of rate constants. Flux-based approaches also do not use the law of mass action – the basis of thermodynamics – at all. Instead, the methods are based on fitting rates without regard for reactant or product concentrations. However, this convenience also limits the predictive power of the methods in that metabolite levels are difficult to predict from flux values. Further, flux-based methods do not provide information about energy costs of pathways, sets of pathways, or organisms. Ideally, the modeling of metabolisms would use kinetic simulations; however, these studies would require knowledge of thousands of rate constants involved in the reactions. In addition, measuring rate constants is labor intensive and thus are unavailable for most enzymatic reactions.

An alternative to both of the above approaches is to model metabolisms using simulations of states rather than simulations of reactions, in which the state is defined as the set of all metabolite counts or concentrations. While kinetic simulations model reactions using the law of mass action, states are modeled based on likelihood ratios of mass action. Both approaches provide information about the energy requirements of metabolic reactions and pathways. However, modeling states rather than reactions have the advantage that the parameters need (standard free energies of reaction) are much easier to determine than the parameters needed to model reactions (rate constants). It is thus necessary to include discussion about recent results, assumptions, and issues in using simulations of state to model metabolism.

Achieving the vision of realistic microbe model communities requires high performance computing. The computations have two major components: simulating both individual cell behavior and interactions among cells and their surrounding environment. The ability to model cellular metabolism accurately and predict outcomes would change the way that we conduct biological research and would lead to advances in biotechnology that could revolutionize material production in industry.

Simulation code for state simulations of metabolism has been written. The code is written in ANSI C and will run on any computer that has a C compiler. Development of the code required us to define probabilistically the relationship between chemical kinetics and thermodynamics for coupled reactions from the perspective of statistical mechanics, which we were able to do. Understanding the probabilistic relationship between the two qualities was essential for elucidating the assumptions in the state-based simulation approach.

A model system consisting of 10 coupled reactions has been simulated both kinetically and using the new state-based approach. We are currently working on scaling up the methods to apply the simulation technology to an independent model of the metabolism of bacteria. However, our developments have gone beyond technology to model biological systems based on their states. We have additionally made progress towards including kinetic simulations of different types. Various biological models require unique simulation approaches, which actually have significant overlap in their computational routines.

To achieve this flexibility and the computational performance that the methods will require, we have developed a high-performance acceleration framework for multicellular biological system simulation, *Biocellion*. This simulation allows its model developers to provide the specifics of their biological system and then accelerates the common computational routines using a high-performance parallel computer. To this end, we tested the framework on moderate-sized clusters (500+ cores) to simulate biological systems up to hundreds of millions of cells. The remaining task is to integrate the state-based thermodynamics cell model to the framework and to scale up the framework to run on leadership class supercomputers to simulate billions to trillions of cells.

For FY 2013, we plan to develop further the state-based simulation code and couple this code to the HPC framework using *Biocellion's* interface. The state-based methods will be developed to understand more fully the assumptions in the models. The methods for accelerating the construction of models will also continue, as model building is often the research bottleneck.

PN12016/2417

Cyber Security Experimentation and Repeatability

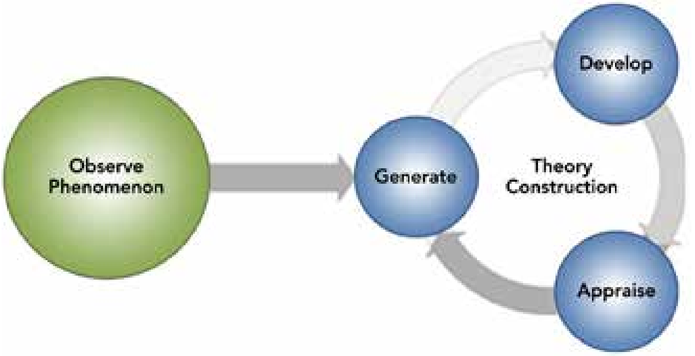
David Manz

This project attempts to introduce scientific rigor into the cyber security research field, which can lead to not only a better understanding of the operational cyber security state but also more informed cyber security decisions.

Workable datasets and metrics are highly sought after by scientists in cyber security. Specifically, datasets are necessary to enable research experiments to test, validate, and answer scientific hypotheses surrounding methods to detect, prevent, deter, and respond to cyber threats, vulnerabilities, and exploitation. There have been few efforts to generate expansive, realistic datasets for the cyber-related research community, and it is often difficult to collect data from actual cyber security events because of potential liabilities.

We propose to use capabilities and technology to generate datasets that cover research and financial computing environments. Using these datasets, we will investigate the characteristics of solutions to generate representative comparative metrics for determining the solution effectiveness. Our objective is to develop or discover methods of performing sound cyber security science. A small core group within the cyber security field has realized and vocalized that our discipline is caught in a cat-and-mouse game between the defenders and attackers, but the defenders are losing ground. This project attempts to build a methodology to conduct fundamental research in cyber security and produce generalizable results. Our ultimate goal is to generate a cyber security science methodology to catalyze the field to perform more scientific research as well as to research a testbed capability to support that research.

We started this year by identifying an interdisciplinary team of researchers in the cyber security field. To accomplish this task, we hosted a series of meetings to discuss the concepts of leveraging scientific approaches from other fields to be applied to cyber security science. Our discussion culminated in a research paper that identified scientific approaches in the social and physical sciences relevant to cyber security. These efforts led to a smaller team, which identified a promising scientific approach. We extrapolated from a means of constructing theories in a life-cycle approach: theory generation (inductive), theory development (abductive), and theory appraisal (hypothetico-deductive).



Cyber security science methodology.

Cyber security science has focused on experimentation, a crucial step in the scientific process, but it alone does not make a science. Experimentation devoid of formal study, theoretical understanding, and scientific prediction can never be construed a valid science in and of itself. Our efforts have led to a fledgling approach to begin the generation of a cyber security body of knowledge rooted in scientific methodology. The mechanics aspects or computers fit well with the experimental nature of physical sciences, but the unique, often adversarial nature of cyber security lends itself to a social sciences study philosophy. Therefore, we defined a hybrid methodology for cyber security science which is a feedback loop that joins methods from both the physical and the social sciences. This approach injects scientific rigor into the field's current research environment.

Our survey efforts were detailed in a paper that was accepted to the Learning from Authoritative Security Experiment Results (LASER) workshop. In addition to the acceptance, they asked us to chair a panel on this important topic, and a small group from PNNL attended the event.

In addition to our efforts to define a cyber security science, we have improved the capabilities of the PNNL CyberSec testbed in supporting scientific experimentation. CyberSec is a multi-purpose, multi-user cyber security testbed that is a part of PNNL institutional computing, a laboratory-wide approach that focuses on consolidating laboratory resources. Our work reduces the time a researcher needs to spend configuring machines and wiring racks, which enables the scientist to spend more time designing experiments and analyzing results.

For FY 2013, the PNNL laboratory-wide Asymmetric Resilient Cyber Security approach will be implemented, and parts or all of this effort will be supported under that effort for the next several years.

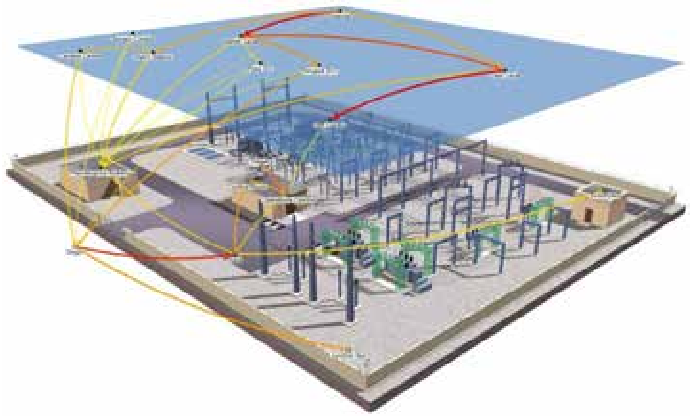
PN12018/2419

Cyber/Physical Security Vulnerability Assessment Integration

Douglas G. MacDonald

This project evaluated physical and cyber vulnerability analysis (VA) techniques and provided a strategic approach to integrating the interdependent relationships of each into a single capability that enabled increased identification and assessment of the true 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 produced a new methodology to blend the independent VA techniques, cross-trained subject matter experts (SMEs) who understand the potential effects each domain can have on the other, and transformation of the existing suite of software tools currently utilized in the physical protection world to identify and assess more accurately the risk associated with a blended cyber/physical attack scenario. This new approach will allow the security analyst to determine a more accurate measure of risk than is currently accounted for in most vulnerability assessments.



PACRAT output summary showing the attack pathways used in both the physical and cyber layers in a given scenario.

Our first task was to evaluate each of the physical and cyber security VA techniques and provide a single strategic approach to integrating the interdependent relationships of each into a single VA capability. The second step was bringing together cyber and physical world SMEs to develop a “common language” by clarifying the various meanings of key terms shared between the two domains. With similar verbiage and a better understanding of system-level interactions, the SMEs applied these creations into a blended system framework for analysis and conceptualized how each element was affected by neighboring elements in the overall framework. This includes how protection elements in one domain can be degraded by attacking a safeguard in the other. Understanding these component-level dependencies ultimately provided a more accurate prediction of vulnerabilities associated with the composite system.

The four potential attack modes evaluated consist of the physical only, cyber only, physically enabled cyber, and cyber enabled physical. 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.

The prototype software tool was designed to capture the new methodology and both accurately model and quickly assess each potential pathway to the target, identifying each sub-system vulnerability and how it could affect the overall protection of the asset. The new Physical and Cyber Risk Analysis Tool (PACRAT) 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 that would reveal 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 “backtrack” to exploit this weakened state in the other domain. This tool analyzes every potential pathway from off site to the target, accounting for sub-system and component-level interdependencies. The tool’s output is a visual and statistical representation of each potential pathway intended to highlight elements commonly exploited in successful attacks.

The results of this tool can be used to guide security investments by improving the system effectiveness on the most vulnerable paths and improve the overall security posture by running “what if” scenarios. 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.

PN11016/2338

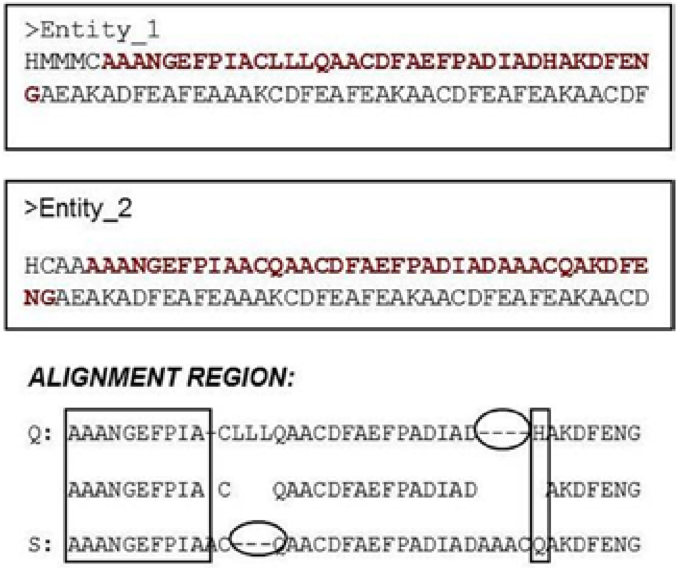
Data-Intensive Algorithms for Bioinformatics-Inspired Signal Detection

Christopher S. Oehmen

This project is developing a general purpose method for discovering sequence-based signatures for use 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 to defend the DOE complex requires analysis of an enormous, ever-growing body of digital information to identify increasingly sophisticated attempts at infiltration and exploitation. To make matters worse, in this environment 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 discovery and analysis of signatures 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. This allows us to discover 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.



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.

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. In FY 2012, we explored more complex representations of the signatures of interest including graphs and profile-based models.

Graphical representation of cyber entities. We investigated different mechanisms to compare graphs and ways to decompile binaries into graph representations. Executable binaries were compared for similarity using an off-the-shelf disassembler that yields a graph-like set of relationships between all the parts of the code. With this, we evaluated several graph distance metrics to identify which one(s) best recognize when executable binaries are related. We determined that edit distance provides the best comparison and a means to construct signatures of change between revisions of binaries. However, edit distance is a complex calculation that does not scale well with increasing graph size, so an approximation method had to be initiated. After evaluating several graph distance approximations, we found the star method to give a reasonable estimate of upper and lower bound of true graph distance. We implemented the star graph and used a Gaussian mean of the upper and lower bounds of graph size as our measure of similarity.

Profile-based models. Historically, these models have been used to represent complex dependencies between biomolecule subsequences. These profile-based models can also be used to more flexibly recognize new (previously uncharacterized) members of the family. In FY 2012, we used sequences generated by our method and recognized to be in a family to build profile-based models. We then conducted pilot experiments to determine the feasibility of using profile-based models to analyze signatures that drift. After converting several versions of an evolving software binary to our string representation, we built sequence-based and profile-based models of a functional family and assessed the performance of those models. We found that both sequence- and profile-based models performed well on recognizing new variants of some software families.

We will follow this pilot experiment with a more rigorous experiment suite in FY 2013 to uncover the conditions under which sequence- and profile-based models capture signature drift.

PN11019/2341

Developing Functionality and Performance Enhancements to the Global Array Toolkit

Bruce J. Palmer

> *We are 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.*

GA is the premier data-centric programming model developed in conjunction with NWChem at PNNL, has been used on most of the large-scale supercomputers deployed to date, and is under active development at PNNL. The 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. Despite GA being 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 (i.e., TETHYS). This limited application base is a concern because further development of GA would benefit from a broader range of requirements. Thus, this project incorporates GAs into several applications that represent a large, diverse group of computing problems with the goal of using these implementations to understand the scaling behavior of GA within multiple 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 2012, progress was made in all four application areas, as detailed below.

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 MPI-based Hypre solver library. We have modified the previous implementation so that the GA-based algorithm approximates the data layout of the Hypre implementation and reduces communication. Both blocking and non-blocking implementations have been developed. Hypre implementation is currently faster than GA, based on scaling studies on PIC. We are currently attempting a more in-depth analysis to understand the origin of performance losses relative to Hypre.

Semi-Empirical Electronic Structure Code. Coulomb interaction contribution to the Kohn-Sham matrix in the CP2K electronic structure code is being converted from its original replicated data implementation using MPI to a fully distributed algorithm using GA. The original algorithm has been modified so that the calculation is decomposed into pair interactions between spatial blocks to reduce latency costs in communication. Additionally, the algorithm has been verified to give numerical correctness and competitive performance with the original MPI code. Currently, we are working on scaling the algorithm to large core counts.

Reactive Chemistry and Particle Tracking. The particle tracking algorithm has been parallelized and incorporated into the TETHYS continuum fluid dynamics code. Efforts are currently underway to combine this capability with the bacterial communities 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 was converted to use GA for the ghost cell updates that are a core part of the algorithm. For FY 2012, we added a non-blocking ghost cell updates operation to GA and combined it with a two-phase update of the LB cells so that we could attempt to overlap computation and communication in the lattice Boltzmann algorithm. Splitting the LB updates into an inner and outer part resulted in a loss of performance that outweighed the communication gain but we are currently looking at improving performance of this kernel to increase overall code performance and scalability.

The bulk of the work in FY 2012 has been focused on implementing new algorithms in the target codes and has positioned us to finish our tasks in FY 2013. Most of the effort in FY 2013 will be oriented towards evaluating and improving the algorithms developed thus far. These include the non-blocking ghost cell updates in the lattice Boltzmann model, the completed microbial communities model in TETHYS, the distributed electrostatic contribution to the Kohn-Sham calculation in CP2K and an evaluation of one-sided versus message passing based communication in sparse matrix calculations. We will also continue our outreach and educational activities to promote further use of Global Arrays in HPC applications and to determine what new functionality and performance enhancements need to be incorporated into the GA toolkit.

PN11021/2343

Development of Parallel Multi-Reference Coupled Cluster Capabilities

Hubertus J.J. van Dam

This project will bring out extreme levels of scalability available in principle in multi-reference coupled cluster methods. The resulting implementations will 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. Previous projects have demonstrated that these methods can be implemented in a highly scalable way. However, single-reference methods can decrease 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, many multi-reference approaches are developed following different philosophies addressing the multi-reference problem and emphasizing various characteristics. These approaches have shown the high value of multi-reference methods for challenging problems. A limitation of current implementations of multi-reference coupled cluster methods is that they have been focused on theory proof-of-concept aspects instead of scalability. Interestingly, multi-reference methods are very promising candidates for parallelization, following from the structure of the equations that allow for two levels of parallelism. One level of parallelism comes from equations associated with a single reference configuration that we have shown can be made to scale well. The second level derives from the fact that all 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 equations for the different reference configurations, as it 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, the project will deliver extremely scalable and scientifically versatile capabilities for studying a comprehensive set of chemical systems.

In FY 2011, we focused on the Brillouin-Wigner multi-reference coupled cluster method, which uses particularly simple coupling terms but has the basic infrastructure for a 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, code scales to at least an order of magnitude more processors than previously reported in literature. We also found that triples corrections are important for achieving highly accurate results, even in the multi-reference case. An analysis of perturbative correction terms was performed focusing on both accuracy and achievable scalability.

In FY 2012, we addressed three main issues. First, the code developed in FY 2011 was modified to exploit the reference level parallelism. For this purpose, the full set of processors is partitioned using processor groups and the reference configurations are distributed across the processor groups. We found that both the Brillouin-Wigner and Mukherjee formulations of multi-reference coupled cluster scale well using such an approach. Second, we added perturbative triples corrections to the single-double code. In this approach, we built on the infrastructure created for the reference level parallelism. As expected, the triples correction improved markedly, and we demonstrated scalability to 80,000 cores on Titan. Third, we considered a number of size-extensivity corrections, important for the Brillouin-Wigner formulation which by itself is not strictly size-extensive. We developed a universal correction for application to multi-reference formulations and showed that this correction significantly improves Brillouin-Wigner formulation results. Finally, we implemented an approach that allows core-level excitations to be treated with multi-reference coupled cluster that offers a new application domain important for the characterization of materials. We presented our work at two conferences, published three papers, and have submitted another paper to a journal.

In FY 2013, we will address bottlenecks in the current implementation. Now that the coupled cluster component scales well, the integral transformation preceding it has become limited in overall scalability and requires restricted communication and memory requirements. Even with improved scalability multi-reference, coupled cluster theory remains a CPU-bound approach; hence, further performance benefits are to be had from applying more compute power to the method. For this, we will revisit GPU developments for which we previously and successfully applied to single reference coupled cluster theory. The final aim for the next year is to perform demonstration class studies to show the strength of these new capabilities.

PN11030/2352

Enabling Hypothesis Driven Research and Discovery in Extreme Data

Kerstin Kleese van Dam

This project uncovers 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 boundaries to exploit extreme data collections by the communities they serve and develop strategies to overcome these boundaries based on methodologies from the aspect of various difference sciences.

In FY 2010, the project broadly evaluated extreme-scale data intensive science requirements of 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 identified a 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. For FY 2011, the project team was extended, and we developed 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 the University of Utah, requirements for a visual data exploration and analysis environment were explored as part of the collaborative discovery environment CAT.

In FY 2012, we further addressed the extreme scale data issues by adopting and bootstraping use of PNNL's Visualization Knowledge (VisKo) approach, which mitigates the variance in service interface descriptions by providing uniform manner of describing data analysis modules, including visualization. VisKo vocabulary is built on the format, type, and parameter concepts and tackles the problem created in the typical use of an implicit, weak agreement that a dataset tagged as a given format adheres to a schema or set of rules used to encode the data into a file. With this rich description of service interfaces, VisKo demonstrated its capability to disambiguate machine's understanding of multiple data structure stored in a single format. Knowing services' format, type and parameter restrictions, machines have adequate information to support automatic discovery, orchestration, and execution of services in collaborative environments. Collectively, work under this project for this year produced five conference papers at various workshops and symposiums and has a pending journal article publication.

PN10033/2275

Enabling the Meaningful Exploitation of Integrated Regional Earth Systems Data

Kerstin Kleese van Dam

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 framework that enables 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 focused on modeling interactions of climate, socioeconomic, 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 different disciplines and backgrounds presents a range of key scientific, computational, and data challenges, such as the following:

- consolidating and integrating overlapping processes consistently across models
- defining scientific relevant exchanges and feedback between models
- dealing with significant variability in spatial and temporal scales
- differing simulation models, programming languages, implementation approaches, and computational requirements
- differing data formats and variable names
- differing data structure, representation, and semantic issues between the unique scientific domains involved.

Thus, the barriers 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 was required 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 “crosswalks” between the disciplines where overlaps exist. They also help 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 be defined only by combining data models.

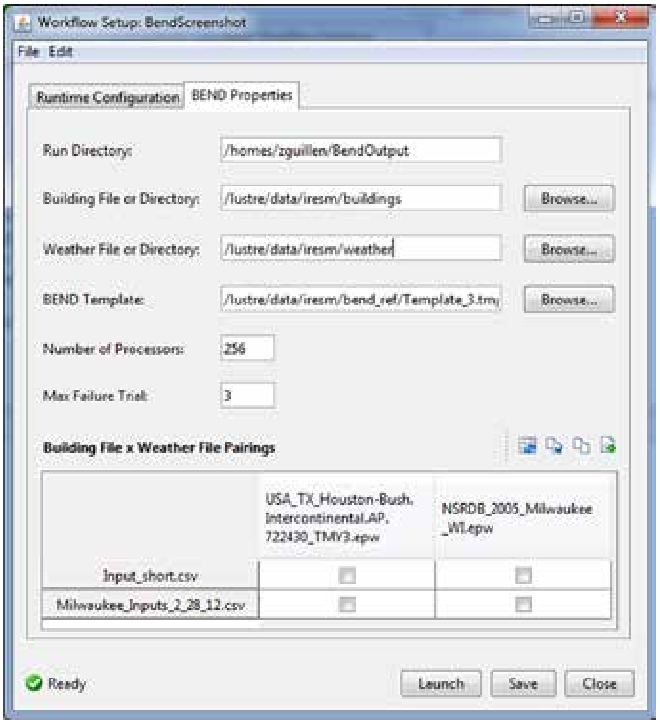
Mid-year, two projects were combined to provide an integrated approach to collaborative model coupling and evaluation, numerical experiments, and modeling framework result evaluation. The projects developed a flexible, hybrid coupling approach that facilitated close coupling of models where possible 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 provided flexibility to include and remove models, as required. Initial implementation work on the loose model coupling began late in the FY, building on the previous project 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, the project built the collaboration infrastructure, extended the MeDICi workflow system, and applied the developed components to create complex scientific workflows in preparation for the multi-scale, multi-domain coupling planned for FY 2013. The project used the existing PNNL-developed Velo software as its core data and knowl-

PN11032/2354

edge management, analysis, and sharing infrastructure. To serve iRESM needs, the following new components were developed.



Run Directory: /homes/zguillen/BendOutput

Building File or Directory: /lustre/data/iresm/buildings

Weather File or Directory: /lustre/data/iresm/weather

BEND Template: /lustre/data/iresm/bend_ref/Template_3.tmj

Number of Processors: 256

Max Failure Trial: 3

Building File x Weather File Pairings

	USA_TX_Houston-Bush.Intercontinental.AP.722430_TMY3.epw	NSRDB_2005_Milwaukee_WI.epw
Input_short.csv	☐	☐
Milwaukee_Inputs_2_28_12.csv	☐	☐

Ready

iRESM BEND model set-up interface.

iRESM Data Model. This content model defines iRESM-specific objects and their relationships as they will be stored in the Velo knowledge base, which has three primary sub-models: the project model, registry, and provenance model.

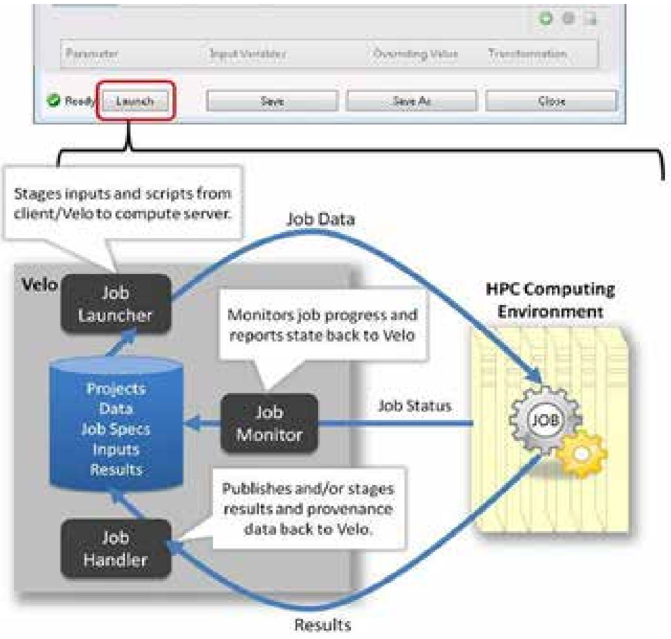
Project Model (Numerical Experiments). Projects are data objects that help scientists to organize their work and encapsulate related data. iRESM created a specific project subtype for numerical experiments that encapsulates all required components, such as workflows, referential data, and any results from simulation runs.

Registry. The registry defines key data types that iRESM added to greatly enhance the provenance graph provided by Velo: datasets, tools, and machines. Each of these types can be versioned and are included in the provenance graph.

Provenance Model. Provenance provides a historical record of what transpired in a numerical experiment and is implemented in iRESM by a combination of metadata saved to objects and a graph of relationships connecting them. When a workflow instance is created inside a numerical experiment, Velo relationships are added, connecting the workflow instance to the workflow definition. As workflows run, status information is conveyed in near real-time and stored as part of the workflow instance metadata. Relationships are added connecting all the inputs and outputs to the workflow instance. A relationship is also added to connect the workflow to the machine on which it ran. Because the provenance model is a part of the overall iRESM data model, any referenced datasets, tools, and machines can be associated with the provenance providing a powerful cross reference search capability, referred to by the provenance community as knowledge provenance.

iRESM Job Execution Components. iRESM streamlined the job execution process for all of the different models and couplings (and upcoming uncertainty quantifications) by invoking all simulations as different MeDICi workflows; therefore, a MeDICi Job Handler was created that was associated with all workflow instances. The MeDICi Job Handler invokes, monitors, and post-processes all running workflows in a consistent manner. Workflows are initiated by remotely dropping a MeDICi workflow bundle file to a monitored folder that serves as a pipeline endpoint. The MeDICi Job Handler parses the MeDICi status log as it is running to update the workflow instance metadata with the current run status and creates separate folders under the workflow instance's Output folder for each run. At the completion of each MeDICi pipeline, the Handler automatically copies the MeDICi status file both to Velo as well as small output files and images. The entire output file set is automatically registered and archived via the Publisher component described below, and a remote link is created inside the workflow outputs folder pointing to the remote data. Any additional post-processing steps used for analysis (such as combining the results of multiple files into a single table) are handled by the pipeline itself as a final step.

iRESM Provenance Components. In addition to adding the Registry object definitions and automatically capturing provenance these new provenance relationships during workflow instance creation and execution, iRESM also developed an Archive component that resides on the computer server. The Archive is a protected area where data (such as simulation outputs) are copied so that they



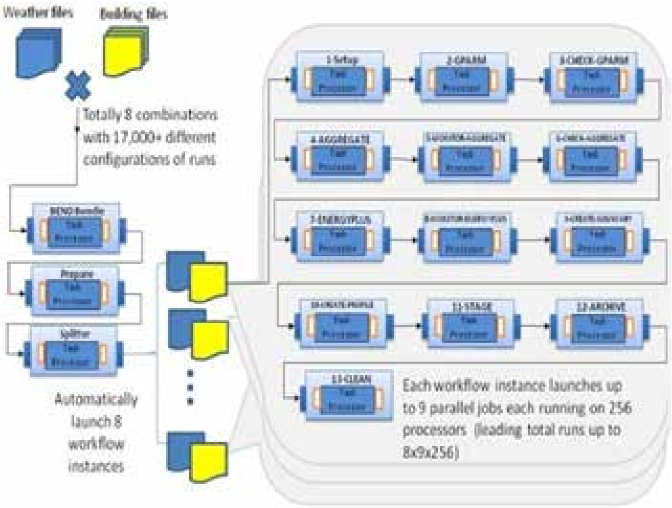
Velo Job Handler and iRESM BEND Job Launcher.

cannot be inadvertently deleted. All remote links created in the knowledge management system point to an Archive location to avoid dangling pointers. The Archive also promotes reproducibility of results in that users can guarantee that they can find the results of a given simulation. It also improves performance as it prevents large data from having to be transferred back to the knowledge management server.

In addition to Archive, iRESM contains a corresponding data Publisher, which is used to publish data to the Archive. The Publisher is implemented as a MeDICi workflow so that extremely large datasets (such as RESM) can be copied in parallel to the Archive, accelerating the process. Every new remote dataset registered via the iRESM Registry View invokes the Publisher to transfer the data to the Archive. The Publisher is remotely invoked as other MeDICi workflows by creating an SSH tunnel and placing a MeDICi configuration file in the file system endpoint folder.

The Velo infrastructure and the MeDICi system were used to develop three basic workflows for specific iRESM models: BEND, RGCAM, and EPIC. For BEND, the project created a more complex high-throughput modeling and analysis environment to demonstrate the capabilities of the infrastructure. The BEND model quantifies energy demands and consumption of residential and commercial buildings based on the characteristics of thousands of different buildings across a geographic area. Representative building type portfolios are created for small geographical regions, within which each represented building type receives energy demand statistics calculated by combining usage statistics with the weather pattern for that geographic area. As a result, scientists have to run the model multiple times to create the energy profile for a larger region.

Using the iRESM infrastructure and workflow systems, the project created an environment where scientists could easily set up, execute, and analyze complex scenarios for BEND. In the numerical experiments carried out by the BEND team, up to 17,000 jobs were submitted in one simple steps, enabling 70,000 jobs run in a short time period. In addition to the benefits of simplifying the set up and execution of the modeling runs, the infrastructure has enabled significant efficiency gains through consistent verification of model results and error recovery procedures for problematic runs.



BEND example workflow set up.

In addition to workflow and infrastructure development, the project developed transformation scripts to be used in workflows that translate climate data into the suitable scale and measures required by other models consuming their information. The core scripts developed where transformations from iRESM to BEND, RGCAM, and EPIC. The team also applied the scripts to convert 60 years of climate data into suitable input files for the aforementioned models.

In FY 2013, we will integrate uncertainty quantification capabilities into the environment and support the initial coupling work of the modeling teams.

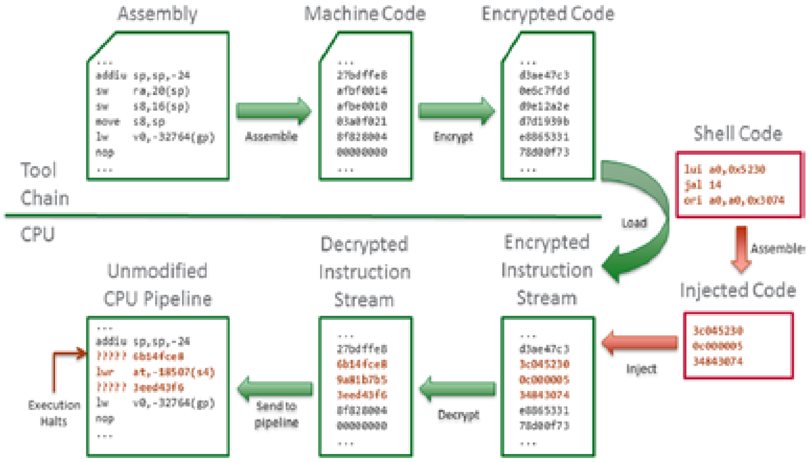
Encrypted CPU Instruction Stream

Richard Griswold

This project seeks to deny adversaries the asymmetric advantage of well-known system architecture in cyber attacks by using instruction stream and program counter encryption to create unique, dynamic system architectures.

While instruction stream encryption is not new a concept with references dating over 20 years, it has not yet been implemented at the hardware layer. Previous studies in this area has demonstrated the effectiveness of the technique, but the research did not progress beyond implementation in software emulators or operating system components. These systems suffered from significantly reduced performance, and the software components themselves were vulnerable to attacks. We initiated this project to research methods for implementing this technique at the hardware layer to increase performance and reduce the attack surface. During the course of this project, we researched the use of program counter encryption as a complimentary technique to provide extra protection against additional attack vectors.

This project has two primary objectives: first, to demonstrate that instruction stream and program counter encryption can effectively defeat several attack vectors, and second, to implement these techniques at the hardware layer. We focused our efforts on embedded systems instead of general-purpose workstations, which gives us a larger variety of processor architectures to work with and much greater hardware configurability. We selected a processor architecture that will allow us to make necessary modifications in hardware, we created a software emulator for this processor to validate our design, and we are currently implementing these techniques in hardware using an FPGA prototype that will be used to conduct experiments to measure the performance, resiliency, and effectiveness of these techniques.



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sw    s8,16(sp)
move  s8,sp
lw    v0,-32764(gp)
nop
...
```

```
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afbe0010
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lw    v0,-32764(gp)
nop
...
```

Code injection attack attempt with instruction stream encryption enabled

In FY 2012, we selected Plasma, a MIPS-compatible softcore processor, as the target for our prototype, and successfully implemented both instruction stream and program counter encryption in a software emulator. We modified the GNU tool chain (compiler, assembler, linker, and associated utilities) to support creating binaries with encrypted instruction streams and to support additional instructions needed for program counter encryption. The software emulator and modified tool chain have allowed us to validate our designs by running test programs and an operating system, including a network stack and web server, with the entire instruction stream encrypted and program counter encryption enabled. They have also enabled us to test caching techniques for improving performance and measure effectiveness against two different attack vectors: code injection and data injection.

These tests demonstrated that instruction stream and program counter encryption are successfully able to defeat code injection attacks that seek to introduce malicious code into the system and combat data injection attacks that can compromise system security by hijacking the execution flow. Tests have shown that by using a decrypted instruction cache, we can keep system performance impact low – less than 10% increase in test execution times – without compromising security. Based on our emulator modifications, we began modifying the Plasma processor itself to implement instruction stream and program counter encryption.

In FY 2013, we will finish alterations and load the modified processor into an FPGA for validation and further examination, including a full battery of performance, reliability, and security tests. We will research ways to apply these techniques to more complex processors and operating systems with support for virtual memory, shared libraries, and multiple encryption keys while still providing full instruction stream encryption completely implemented at the hardware layer. We will undertake a more detailed cost/benefit analysis and investigate refinements to instruction stream encryption to provide more predicable behavior in handling improperly encrypted code.

PN12026/2427

Experts Inundated with Data: the Biomarker Problem

Karin D. Rodland

We are developing approaches to improve the accuracy, robustness, and interpretability of signatures generated from high-throughput data by integrating statistical approaches with expert knowledge.

The 'omics revolution in biology has provided investigators with a plethora of complex datasets based on comprehensive molecular analyses with the potential to solve a large number of important problems including treatments for diseases, bioenergy production, and detection of bioterror agents. The field of biomarker identification has been plagued by the problem that either a purely data-driven approach is taken or a largely expert-driven approach is taken. The biomarkers identified from these analyses do not generalize well to larger sets of data, may not be interpretable to a domain expert, and may not show sufficient accuracy for their application.

Our project integrates statistical approaches with expert knowledge, derived from large-scale community annotation efforts and explicit input from a domain expert during the process. This is an important area of research that will allow advancement in this difficult and highly impactful area. We will develop a pipeline for integration of data sources that allows generation of better signatures based on incorporation of expert knowledge. Additionally, we will develop tools for classification and expert feedback on statistical integration processes. We will also work toward identifying more robust signatures of processes for the problems serving as applications during our development process.

In our first year of this project, we developed a pipeline for combining statistical analysis with expert knowledge to identify biosignatures from proteomic data from a mouse model of chronic obstructive pulmonary disease. These biosignatures are capable of accurately classifying samples based on their disease state. The process involves use of Bayesian integration, clustering of proteins based on functional annotation (expert-derived community knowledge), and allowing the expert to participate in the process through a sophisticated and intuitive data exploration tool. Additionally, we developed methods for statistical analysis of data with non-random missing values and generated a dilution series proteomics dataset to serve as a gold standard for rigorous evaluation of protein quantification methods. We have developed the Data Cognostics Tool, which allows experts to interact with the signature identification process by visualizing, ordering, grouping, and filtering individual features used in classification (in our initial application, proteins).

In FY 2012, we performed data pre-processing by designing a dilution series for mouse plasma proteomics, ran these proteomic samples, and completed an initial quality analysis on the resulting dataset. This dataset will serve as the first high-quality gold standard dataset generated specifically to evaluate the protein quantification problem. Additionally, we completed work on a proteomics data pre-processing pipeline, including quality assessment, normalization, and protein quantification using trend analysis. This work serves as the basis for our proposed work with the gold-standard dilution series dataset. Finally, we developed a method for principal component analysis on data with non-random missing values and have a manuscript on this under review. In addition, a portion of this work appears as an article in *PLoS Computational Biology*.

We will complete our biosignature generation pipeline then apply it to two independent problems. The first is large-scale patient data from ovarian cancer and will be funded in part from the existing CPTAC project. The second will demonstrate the application of the pipeline outside the biological domain to a cyber security dataset. We will develop a signature for classifying session activity (malign versus benign) from statistical and expert-based relationships between event series. Additionally, we will complete work on a proteomics dilution series that was generated in FY 2012 to serve as a gold standard for protein quantification. Finally, we will continue to work on developing capabilities of our Cognostics tool.

PN12028/2429

Extreme Scale Capabilities for Subsurface Science and Engineering

Steven B. Yabusaki

This project is creating an enduring, high quality software that provides easy maintenance of capabilities under evolving hardware and software environments, extensibility of capabilities by domain scientists, modular replacement of code components, and portability to accessible computing architectures.

We are expanding eSTOMP application capabilities by providing the supporting software infrastructure for extreme-scale computing. The new simulation capabilities will include geomechanics, fully integrated well models, genome-scale models of microbial metabolic pathways, and unstructured mesh discretization. The large-scale and comprehensively detailed applications that are targeted will require considerable software engineering to achieve robustness, scalability, performance, and fault tolerance on existing and future extreme scale computing architectures. Significant issues that will be addressed include solver performance, load balancing, scalable I/O, and memory management. A key component of the project will be algorithm development to exploit non-uniform memory access and heterogeneous accelerator-based architectures (e.g., GPUs).

The new capabilities and infrastructure will enable applications of unprecedented magnitude and process model detail. Large-scale, nonisothermal, multiphase flow and geomechanics simulations of deep geologic carbon sequestration will be used to assess the long-term impact of large arrays of supercritical CO_2 injection wells on CO_2 migration, porewater displacement, and caprock integrity. In conjunction with recent advancements in subsurface sampling that can determine a wide range of metabolic process activities by their association with genes, proteins, and peptides from specific microorganisms, the integration of *in silico* cell-scale metabolic models into the eSTOMP coupled process subsurface simulator will provide a mechanistically detailed representation of the intracellular metabolic pathways and environmental exchange reactions under realistically complex subsurface conditions.

This project was terminated in early FY 2012 upon re-prioritizing of laboratory-level scientific issues and reallocating investments. Prior to that end, the following progress was made:

eSTOMP-WR. The isothermal single-phase eSTOMP-WR simulator ran the first full implementation of a comprehensive genome-scale metabolic model for *Geobacter metallireducens* coupled to 3D variably saturated flow and multicomponent biogeochemical reactive transport in a physically and geochemically heterogeneous aquifer undergoing engineered uranium bioremediation. The cell-scale physiology represented by a physico-chemically constrained network of 697 intracellular and 51 environmental exchange reactions was solved for every iteration of every timestep for every grid cell using linear programming optimized for maximum growth. The simulation was run on EMSL Chinook using 1024 cores for 15 hours.

For many applications, including the one above, the reaction network solver in eSTOMP consumes over 90% and sometimes over 99% of the computational effort. While the eSTOMP reaction solver has been engineered to scale near linearly, the large computational effort was shown to be amenable to further efficiency using GPUs. The first eSTOMP prototype with CUDA programming for the reaction solver has shown that the combined CPU-GPU resource can be used effectively to reduce the total computational time. eSTOMP-WR is one of three existing simulators being used in a high-level DOE project that is developing the next generation subsurface simulation capability for environmental management.

eSTOMP-CO_2e. The nonisothermal, multiphase flow and brine transport eSTOMP-CO_2e simulator for supercritical CO_2 behavior in deep geologic systems was updated to improve convergence using developed techniques. A geomechanics capability for eSTOMP-CO_2e has been successfully tested for elastic behavior. Development and testing of the coupling with plastic behavior is ongoing. eSTOMP-CO_2e is slated to be used in the U.S. Environmental Protection Agency's regulatory role for carbon sequestration.

eSTOMP-WAE. Development of the GA/grid component engineered non-isothermal, multiphase flow and transport operational mode, eSTOMP-WAE was completed and tested against the STOMP test suite. This was the third eSTOMP operational mode to be created using the GA-Grid Component. eSTOMP-WAE will be used in the assessment of dessication approaches for attenuating the transport of Tc-99 and other mobile contaminants in the Hanford deep vadose zone. It will also be instrumental in the modeling of carbon and nitrogen fluxes via surface vegetation and hydrological processes coupled to biogeochemistry in variably saturated near-surface systems.

PN12032/2433

Geological Sequestration Software Suite Framework

Ian Gorton

> ***We are designing, developing, and deploying a software framework with effective capabilities integral to evaluate and model 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 subsurface domain conceptual model, 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 applied under varying conditions is extensive and difficult to manage. The process is also iterative, leading to tens and thousands of simulations run for a single site. Organizing, managing, and tracking data at each stage are critical to analysis integrity, verifiability, and repeatability yet is ad hoc, time-consuming, and error prone.

In this project, we are designing and creating novel provenance capture and analysis, and tool integration frameworks for carbon sequestration modeling. These capabilities will provide the ability to track data and assumptions in a given model, and make available a broad toolset 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.

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 CO_2 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 as many face challenges similar to carbon sequestration. For example, many need the ability to parse large volume of initial data, document missing data and assumptions, and track of data used throughout the project life cycle.

Velo architecture.

In FY 2012, we continued to add and improve many GS^3 features. In particular, we:

- updated to newer version of underlying GS^3 technologies (Mediawiki and Semantic Mediawiki) that provides GS^3 with the latest security updates and improved APIs for integration with external applications
- improved many core functionalities such as tree-based file navigation, copy/paste functionality through web interface, rich text editor for user annotation, and editor for ASCII files within the wiki
- added the ability to launch tools on a collection of files in scratchpad and copy or create soft links to the files into a new directory
- added support for running task parallel jobs on PNNL Institutional Computing clusters, enabling us to integrate and demonstrate parallel uncertainty quantification (UQ) runs developed under the UQ project
- provided a new interactive provenance graph interface through which users can walk the provenance graph to explore various captured relationships
- created an initial version of the STOMPInputAdvisor tool, providing users with appropriate reference documents and code snippets to guide them through STOMP input file generation.

In FY 2013, we will continue to improve provenance graph, STOMPInputAdvisor, and the job monitoring tools. Because FY 2013 is the final year of the GS^3 project, we will create documentations such as user manual and help pages. We will continue to modularize code, making it easier to separate core GPL components from possible non-GPL extensions.

PN11036/2358

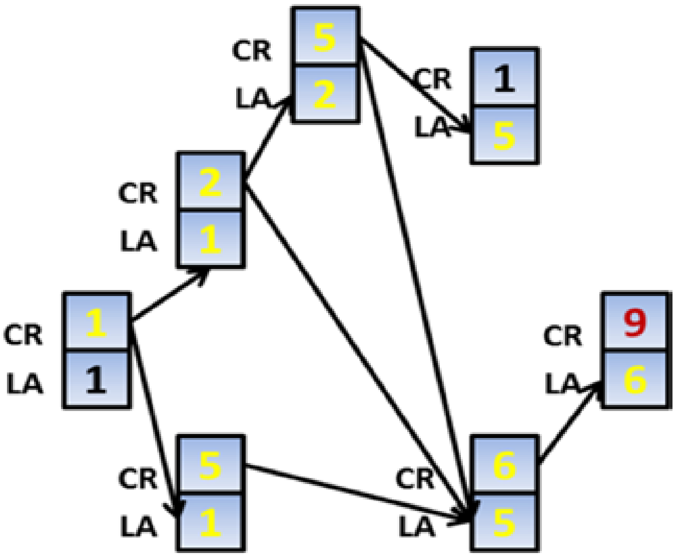
GRADIENT: Graph Analytic Approach for Discovering Irregular Events – Nascent and Temporal

John R. Johnson III

This research addresses the challenge of detecting time evolving signatures in large volumes of data using one or a few passes on the raw data. Our approach will be to reduce the data size by reformulating the problem in a graph theoretic or sparse matrix framework and then leverage novel high performance computing platforms to mitigate the increase in complexity.

The past several years have seen a renaissance in the study of graphs – or networks – and the development of graph analytics spurred by increased interest in social networks and the growing importance of engineered networks. Innovative new technologies such as the Cray XMT supercomputer have been designed explicitly to support graph analytic computation and are effective on irregular problems found in graph analytics. In addition to naturally occurring graphs, graph approaches can solve challenging scientific problems in very different fields, ranging from graph-based 3D flow field visual analysis to bi-simulation for discrete, continuous systems. With the continuing explosion of data across the scientific and analytic community, new approaches are required that can find appropriate, compact representations of underlying data to support discovery and analysis.

Our research will advance the current state-of-the-art by using a graph analytic approach to support signature detection and analysis on extremely large, dynamic, streaming data sets across a broad range of domains. We will use large-scale graph analytic techniques to enable dynamic signature detection in massive data sets. The uniqueness in our research is reducing the raw data by transforming the signature detection problem into a graph representation and using large-scale graph analytic techniques and specialized, high-performance computing platforms to tackle this problem.



Reachability graph for pass-the-hash attack

In FY 2012, we focused on detecting the signature of a specific cyber attack against an enterprise called *pass-the-hash*, which takes advantage of vulnerabilities in Microsoft Windows security. We identified, catalogued, and described ten distinct PNNL data sets that could be used for this activity. The first phase of the project focused on three of these data sets: Windows event logs (6TB), firewall data (28TB), and internal network flow data (9TB). From the event logs, we converted the data into the DIMACS-9 graph format. In this process, the data were reduced to 15% of their original size.

We gathered statistics on the graph using variable size time windows and variable time steps to characterize its structure. Statistics included average out-degree, number of edges, number of vertices, diameter, maximum out-degree, and average clustering coefficient. We also developed algorithms using randomization techniques to perform matrix operations on subsampled matrices of smaller size while minimizing error. The approach we used was to coarsen the graph using Graph Minors, which enabled us to preserve walks in the graph, an essential feature to help detect the signature we wanted. This allowed additional data reduction without loss of fidelity.

Results from this research were presented in an invited talk at International Supercomputing in Hamburg, a mini-symposium at the SIAM General meeting in Minneapolis, and have been submitted to the CSIIRW workshop at Oak Ridge.

In FY 2013, we will focus on developing techniques for *automatic* recognition of evolving patterns, triggered by operations such as those identified in the *pass-the-hash attack*. These automatic techniques will be analyzed to characterize whether and under what conditions the recognition can occur fast enough with respect to the attack to provide an opportunity for mitigation. While the majority of the work in this research will be forensic in nature, a goal will be to understand what the gaps are in moving to a near-real time environment to potentially enable future predictive signature detection. We will extend the basic results to other problems within cyber security and will also extend to other domains.

PN12037/2438

Identifying Cyber Assets and Inferring Criticality

Tom Carroll

Understanding the relationship of cyber assets to business processes is critical for maintaining and securing large enterprise networks. In this project, we investigated methods to determine cyber assets, discover dependencies between assets, and evaluate the importance of the asset to the enterprise.

Large enterprise computing environments are shifting to a paradigm in which operational tasks are dynamically and ephemerally allocated to cyber assets. The only constant in these environments is change; thus, cyber analysts, defenders, and operators currently have difficulties assessing situations in today's "static" dynamic, evolving environments such as those proposed for moving target infrastructures that will only complicate their roles. Further, a mismatch of which assets business operations considers critical and what computer and network operations considers critical impacts the availability of resources, causing both direct and indirect costs to the enterprise.

Cyber assets are allocated to business processes to complete tasks. They are not just physical components such as computers, routers, and switches; they include staffing, facilities, threads of computation, and information. Formally, the criticality of the asset is derived from the relative importance of the business process. Unfortunately, few enterprises expend the time and resources necessary to develop their business model that identifies and assigns importance to their organizational objectives. If they do develop the model, it is often too abstract to be of operational value. Many methods of asset identification and criticality evaluation exist, but these approaches are largely pen-and-paper exercises. The goal of this project was to investigate methods that will dynamically and rapidly discover cyber assets and the relationships between them, perform identification, and assess the criticality of each asset in relation to the enterprise's business processes.

Before assets can be associated with their respective business processes, the assets must first be discovered and the interrelationships between them mapped. Asset discovery is a continuous process that learns the state of the network as it evolves. Because cyber assets encompass a large number of entities, we focused on discovering and identifying network services. A network service provides defined functionality to members of a network. A service is then defined into terms of the requestor, responder, and the channels by which the pair communicate. While methods to discover services can be broadly grouped into network- and host-based approaches, we determined with the support of subject matter experts that network-based approaches are preferred. Host-based approaches require running an agent on each system. Agents are intrusive and impact system performance, and in this era of employees bringing their own devices to work, deployment on all systems is improbable. We determined that a combination of network-based passive and active discovery approaches are necessary to ensure that most services are discovered and properly identified. Passive discovery identifies entities by examining patterns of communication or listening into communications, while active discovery probes services by interacting with them.

We investigated network-based approaches for dependency discovery. A network service "A" depends on "B" if "A" is unable to complete its task without "B." The algorithm for dependency discovery is based on the following observation: a server must initiate requests to and receive responses from upstream servers before it can complete its task and respond back to the client. The benefit of this intuitive approach is that it is less dependent on being "tuned" than previous algorithms. Concurrent requests and caching do cause problems for the algorithm. The difficulty with concurrent requests is solved by large sampling sets. Rare accesses are discovered by understanding what causes these accesses and specifically searching for those patterns that encompass the communication. The record sets generated by NetFlow, the *de facto* network profiling protocol, are ideal for this algorithm.

While there are several methods to establish the identity of assets, most of these techniques rely on channel properties (e.g., summary protocol information) to identify a service and, therefore, brittle. We investigated a robust approach that combines a set of heuristics into a Bayesian network. By appropriately setting the virtual evidence on the appropriate node, we can identify a service with associate measure of certainty, and we can improve our certainty by actively network probing the service.

Finally, we associate the business process with its supporting cyber assets. Business operations understand the importance of business process; this information rarely communicated to computer and network operations. Using an extension to business process model and notation, business operations assess the criticality of the business task and note known cyber assets that are being employed. Combining known assets with the output of the dependency discovery permits us to identify all assets that are employed in support of that business process. The priority assigned to the business process is used to derive the criticality of the asset.

PN12040/2441

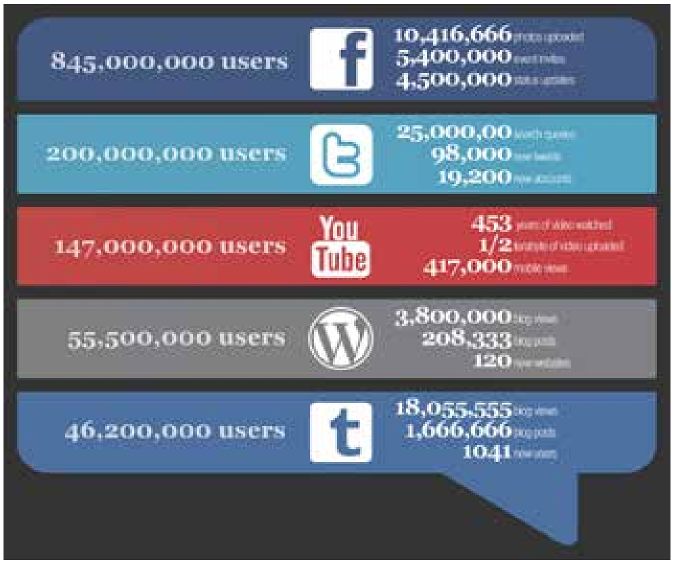
Immense Social Media Stream Analytics

Courtney D. Corley

Today's analysts need methods to identify and monitor significant events efficiently and measure their effects as expressed through social media. Knowing how social media is used during and in response to anticipated and unanticipated events (such as natural disasters, disease outbreaks, speeches, elections, and crises) enable more accurate measurement of the potential effect of those or similar events and informs planning and response decisions.

Existing analytic methodologies do not accommodate the innate characteristics of social media – they are limited by the inability of existing computational methods and systems to process the immense volume of data in real-time and the inability to cope with intentional or unintentional message attenuation such as spoofing, damping, and thematic and lexical drifts. These types of analysis methods on social media streams remain a capability gap.

Our research will develop methods that identify and provide access to analytically informative features, such as trends and transitions, key terms and topics, and events and entities. This computational advancement will augment the abilities of analysts by providing them with complementary capabilities for analyzing social media streams. In addition, this project leverages PNNL's institutional computing platform (currently configured with over 600 nodes, 32 cores and 64GB RAM per node, Lustre file system). To develop our algorithms and framework, we are utilizing over 10 billion social media posts including tweets, blogs, microblogs, mainstream news articles, forums and classified ads. From these, 60% are in English and the other 40% are distributed among at least 60 languages.



2012 social media statistics.

In FY 2012, we developed unique analytics methods – 34 in total – that span traditionally social media analytics to novel advanced time-series and event forecasting methods. For example, the temporal analytic methods to 1) transform semi-structured data to a time series; 2) measure distance between time series; 3) interpolate missing data; and 4) decompose time series into seasonal, trend and other effects. The value of these methods is that they now enable the discovery of signal attenuation and misdirection in social media. To develop the analytic methods, the project team engineered and developed a Computational Sensor Platform to ingest source-agnostic streaming multi-mode data (>2MB/s). Next, the team engineered and developed a distributed database, which enables analytics on massive semi-structured data at interaction speed.

We will research methodologies for cutting through the platform noise, resolving message attenuation, leveraging proven techniques, and collaborating with users to ensure we provide analytically useful insight in to immense social media streams. The development of these computational methods at scale will enable the identification and characterization of behaviors within social media and the measurement and impact of these behaviors within social media. Additionally, we will develop visual analytic methods to provide access to these computational methods and to support understanding the phenomenology of social media.

Ultimately, by enabling discovery and exploration of behaviors within immense social media streams this research will empower analysts to anticipate and monitor crises and assess their impacts to the security of affected people and infrastructures.

PN12042/2443

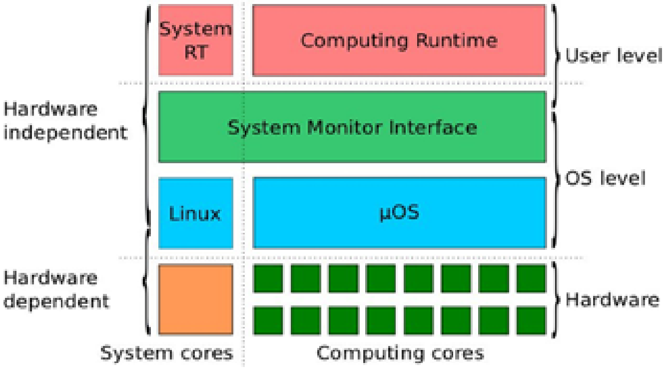
Integrating Advanced Optimizations for Extreme Scale Systems

Adolfy Hoisie

> ***Achieving exascale performance with a limited power budget is essential to ensure scientific progress is many areas, including biology, chemistry and national security. To this extent, an automated and concerted approach between hardware and software is necessary to ensure the most efficient use of resources.***

Limitations on energy consumption, uncertainty about technology, poor reliability, and programming difficulty form a daunting challenge for exascale systems. Currently, these problems are addressed manually by programmers or system administrators. However, burdening the programmers with managing low-level details is counterproductive and overlooks the benefits and capabilities of the exascale system. An automated system that accurately collects information at runtime and provides actionable tools to improve system's steer performance and power consumption is necessary to ensure the most efficient use of resources.

This project focuses on one essential aspect of the automation of system management so that an exascale system will operate at the most efficient level. Specifically, we will develop a performance and power steering capability that collects at runtime information pertinent of program behavior; generates a dynamic model of power and performance based on this information; and verifies, also at runtime, whether the application's performance and energy use expectations are within desirable range. Our research advances that are enabled by this work are multiple. We will design a general methodology for dynamic power and performance modeling, significantly advancing the state-of-the-art in this area. Additionally, we will design a monitoring system that generates the requisite application and system information with the applicability to a range of exascale architecture. From these tasks, we will be able to validate the results through the implementation of an instrumented runtime system that allows to "dial-in" various performance and power knobs.



The SMI and RTM systems.

In FY 2012, we designed and developed two basic system layers: the system monitor interface (SMI) and the runtime monitoring system (RTM). The SMI specifies a common interface between the low-level system component (hardware and operating system) that provides raw information and the high-level components (runtime system and programming language) that use the information provided. For example, the SMI exports some performance information to the higher-level system without exposing the low-level detail of the actual hardware performance counters that are used to obtain the information. As an added benefit, SMI ensures portability across different systems.

The RTM constantly monitors the execution of an applications and collects information and statistics that are used to develop a dynamic model of the applications and to verify whether the application's performance and energy consumption meet the expectations provided by the dynamic model. The RTM consists of a specific kernel module designed to effectively perform monitoring with high frequency and low overhead.

SMI and the RTM were designed as a kernel modules to reduce the runtime overhead introduce while running HPC applications. In the event that the applications performance or power consumption are not within the expected range, the RTM signals the user-level runtime system. The implementation of a user-level runtime system for MPI application in work currently in progress.

In FY 2013, we will develop novel methodologies and technique for dynamic modeling. We plan to integrate the dynamic model with the RTM, SMI, and the user-level MPI runtime system. We also plan to develop actionable components that can improve the system efficiency at runtime. Finally, we plan to use the developed system to explore applications' characteristics, performance/power trade-offs, and to use this knowledge to drive the development of exascale runtime systems through co-design.

PN12043/2444

Integrating Power and Performance Modeling for Exascale Systems

Kevin J. Barker

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. The past three years of this project (concluding at the end of this FY) have aimed to address these concerns.

Over the course of this project, we approached the challenge from two vantage points. The first was developing a set of tools to quantify and characterize power consumption of a workload executing on a hardware and software platform. We developed a set of micro-benchmarks kernels that exercise single functions of computing systems (e.g., floating-point computation, memory accesses through levels of the memory hierarchy, and inter-processor communication). The second component was developing a tool suite that could characterize the execution of a workload in terms of these activities. Measuring the power consumed by benchmark kernels and correlating these activities with application characterization, the goal was understanding the power consumption patterns of executing workloads. This is challenging work that requires the availability of fine-grained measurement platforms, which have also encompassed part of this project. The work is ongoing, forms components of newly funded projects, and will continue to have impact.

We developed methods for optimizing application power consumption using tools available today. Optimizing power and energy consumption is not simply a concern of the hardware; methods must be developed for maximizing efficiency at all system levels from the hardware through the system software and application. PNNL is uniquely positioned in this regard, with expertise in various levels of the software and hardware stack. At the hardware level, we explored techniques for modifying power consumption characteristics of devices during runtime (e.g., dynamically altering the voltage and frequency (DVFS) of CPU processor cores to manage more efficiently a finite power budget). For communication software, we explored methods for optimizing energy efficiency of single-sided data transfer operations implemented in the ARMCI communication library. Finally, at the application level, we developed *Energy Templates*, which encapsulate knowledge of per-core application runtime behavior in an analytic model to identify periods during execution to conserve energy. All these techniques work in concert; tools provided by the hardware such as DVFS are exploited by higher levels in the software stack that contain a complete picture of ongoing application activity.

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 an 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. In both cases, as message sizes increase, there are improvements that show reductions in energy consumption. We also leveraged existing relationships with major hardware designers (e.g., AMD and Intel) for access to next-generation hardware and gathering data to characterize applications with different requirements (e.g., compute, memory, and network).

At this same time, we explored GPU accelerator hardware from the perspective of power and energy efficiency. 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 is how GPU hardware fares compared with multi-core CPUs in terms of energy efficiency. With these challenges, we utilized a system in FY 2011 of two Intel 6-core Xeon X5650 Westmere processors (with a clock speed of 2.67GHz) and four Nvidia Fermi C2050 GPUs. Results

PN10049/2291

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 results in improved energy efficiency for the GPU (0.5GF/W vs. 0.27GF/W). However, increasing 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 *Energy Templates* that encapsulate knowledge of per-core application runtime behavior in an analytic model 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, an execution pattern results 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:

- represent an application-specific sequence of active and idle states for each processor core that may vary
- contain rules associated with the transition from one state to another using a model that represents the application's expected parallel activity
- use triggers that enable state transitions by transparently monitoring application activity
- enable the runtime system to make informed decisions about whether to alter an individual processor core's power state.

The power-instrumented NW-ICE machine measured 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 11W power difference per core. With greater differences in power states available on more current and future cores, observed power savings is expected to be even greater than what we have observed here.

The execution time measured with and without *Energy Templates* 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.

Testbeds form a critical component of this work. Accurate measuring power at a suitable resolution requires dedicated measurement resources typically not available at suitable scales. At the start of FY 2012, the PNNL Institutional Computing (PIC) cluster was stood up containing ~20K cores of AMD Interlagos Bulldozer processors connected with QDR InfiniBand. This state-of-the-art system contained instrumented power distribution units able to sample consumption at the power outlet level with 0.33Hz resolution across the full cluster. This represents a sizable increase over previously available resources. We are currently using the PIC cluster to expand our *Energy Templates* work by exploring more applications at larger scale. This work is targeting a publication for the end of FY 2012.

While the PIC cluster is an excellent resource for exploring power consumption at larger scales, a goal of this project was to characterize power at fine-grained temporal resolution. We have the goal of tying power consumption characteristics to application workload features, many of which are at the millisecond or finer resolution. To address this, we have acquired a system of the same architecture as the “quad-nodes” which compose the PIC cluster together with a high-speed data acquisition device. Intrusive instrumentation on the system architecture will allow for the measurement of power consumed by individual components within the system (e.g., CPU sockets, memory) at a very high frequency. By determining how power is consumed by different application phases, we will endeavor to build intelligence into runtime software to optimize power consumption at larger scale. The PIC cluster will serve as a validation platform in this work. This is ongoing work and will continue on other projects funded by external agencies.

This project has yielded important and tangible outcomes, including the development of methodologies for characterizing power, communication libraries optimized for power consumption, and the *Energy Templates* mechanism for facilitating information exchange between application software and underlying runtime software. Looking forward, these techniques and tools will be expanded through the use of testbed equipment and applications of interest to the Laboratory and external agencies.

Intelligent Networked Sensors Capable of Autonomous, Adaptive Operations in the Electric Power System

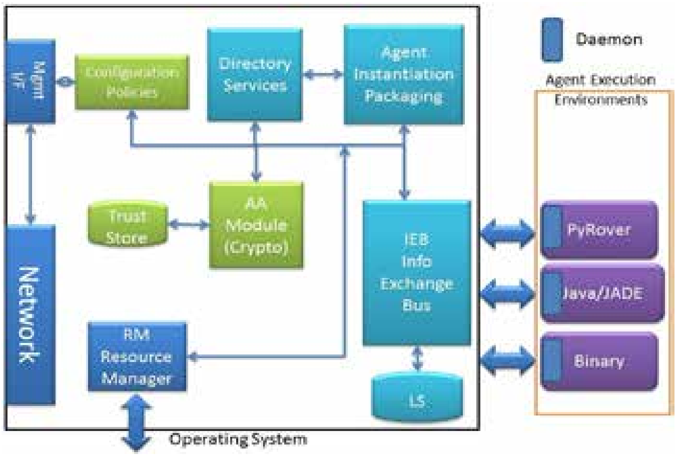
Bora A. Akyol

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.

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.

In FY 2011, we developed the design of our software platform Volttron™, which 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.



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.

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.

During FY 2012, we completed the initial version of the agent platform based on the design document from FY 2011. A paper highlighting the design of our software platform was accepted and presented at the ATES 2012 workshop as part of the AAMAS 2012 conference; we also presented a paper at MASCOTS-2012. The hardware purchased in FY 2011 was assembled into a hardware testbed

Hardware testbed platform.

PN11045/2367

during FY 2012 and used to showcase demonstrations of our software platform, including coordination of plug-in electric vehicle charging and cooperative load scheduling.

As part of the cross-focus activities, we interacted extensively with other projects and chose three candidate projects for integration in FY 2013. In addition, we will complete and harden the implementation of our software platform for potential commercialization and/or open source release. We plan to port the platform to another CPU architecture, such as an ARM processor, and will integrate with algorithms and software developed in other related project focus areas. Additionally, we will work with the PNNL SmartHomes and Grid Friendly EV Charger programs to investigate the feasibility of using our software platform. Finally, we will continue our publishing efforts with the goal of presenting at another agents' conference.

Linear Algebra Solvers and Associated Matrix-Vector Kernels for Power Grid Simulations

Barry Lee

This project researches the development of advanced linear solvers and matrix/vector kernels, key enablers for power grid modeling, through high-performance computing simulations. These advanced solvers and kernels will enhance the modeling capability for current and future power networks that utilize 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 advanced models, to obtain the solutions to these mathematical equations, carefully designed parallel solution procedures that use high-performance computing will benefit the simulation capabilities.

The computational bottleneck of these solution procedures often arises 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 during FY 2012 include examination and development of eigenvalue solvers for small-signal stability problems. Succinctly, these problems analyze the stability of a power grid network under small disturbances about a stable operational point. This stability is determined by finding the eigenvalues of the Jacobians of the power system. We developed and implement eigenvalue solvers with the appropriate transformations and preconditioners for the efficient calculations of these eigenvalues. This task entails the development of solvers for the two general types of eigenvalue problems (i.e., the standard and the generalized eigenvalue problems).

One important stability application, which is relevant in the determination of security margins of a power grid network and where our solvers have shown promise, is a new non-iterative small-signal stability approach. This approach requires the solution of a generalized eigenvalue problem $Ax=\gamma Bx$ and the task is to find the approximate largest real eigenvalue γ. Here, A and B are $(n \times n)$ real-valued but non-symmetric matrices. Since n is large (35,878 for the WECC system), the largest real eigenvalue cannot be found by itself. Rather, a handful of approximate eigenvalues must be found together. We used a shift-and-invert implicitly restarted Arnoldi (SI-IRA) iteration with an appropriate transformation and shift (actually, an a priori shift is first taken, and then it is adapted). The software used was written in c/fortran with different components parallelized in MPI. This parallelization allows us simultaneously to solve the generalized eigenvalue problem that corresponds with several different load choices.

For FY 2013 and with a very limited budget, we will complete our investigation of small-signal stability problems for security boundaries using larger HPC scales (e.g., several hundred cores).

PN11046/2368

Mapping Molecular Dynamics Algorithmic Parallelism to Heterogeneous Architectures

T.P. Straatsma

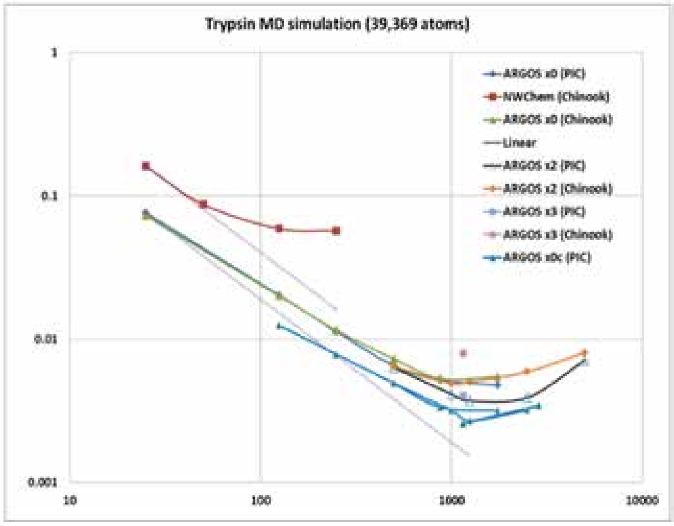
Novel computer science and software engineering approaches are applied to develop a high-performance molecular dynamics (MD) modeling and simulation implementation for biomolecular modeling research.

A principal and general challenge for biomolecular modeling and simulation in support of environmental molecular science involves the generation of extended molecular trajectories. These 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 the 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.

Based on a domain decomposition approach, we have designed a new data structure to exploit locality and reduce communication and memory requirements. Distribution of the workload taking into account the workload based on relative orientation within the physical decomposition allows a number of processes to be used of up to 42 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. This feature is accomplished in part by a new Global Arrays feature put-notify, which provides a convenient means of using a push-data model for communication, instead of the traditional pull-data model.

The approach described above has been implemented in a new MD kernel that in FY 2012 has been extended to the application to heterogeneous systems. Additional optimizations for intra-node parallelism and topology-aware assignment of cell-pairs results in a highly optimized simulation framework capable of achieving simulations of close to 70 ns/day. This is accomplished by communicating data needed by multiple processes on a node only once to that node, using a polling mechanism for each of the processes to determine the availability of the data. This approach is possible as one of the design features of Global Arrays. In the simulations, one core per node is 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. In addition, three processes handle control tasks, such as global accumulation of kinetic energy and virial for constant temperature and pressure simulations as well as with I/O requirements such as trajectory recording. Compared with 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 2013 include the development of multi-ensemble implementations, energy optimization using *Energy Templates*, and the implementation of free energy methodologies.



Wall clock timings for a 39k atom solvated trypsin simulation using the cell-distributed NWChem MD module and the newly designed cell-cell pair distributed kernel.

PN11049/2371

Multimedia Analysis of Cyber Data

Deborah A. Payne

Our approach for cyber intelligence in this project is the creation of a multimedia analytic environment that identifies multimedia similarities from cyber data retrieved from web sites to infer relationships or common interests between entities.

Traditional cyber intelligence is performed by looking for indicators of threats in log data. This analysis has been applied to large structured or semi-structured text data summarizing the activity of a machine displayed in complex spreadsheets without inclusion of the multimedia content accessed. Contemporary analysis tools work with either log data or multimedia content in isolation, which do not provide the analyst with the ability to derive patterns of interest across information silos. The creation of a system that allows analysts to review multimedia data will aid in uncovering patterns that are overlooked when analyzing just the textual data. For example, an analyst might be interested in baking a cake and is searching for the text words flour, egg, and oil. With a multimedia system, the analyst can also search for images of cakes, flour, eggs, and oil.

This work is resulting in the development of approaches for applying multimedia analysis to cyber intelligence. The technical research and implementation are of use to analysts at PNNL and could be applied to a broader audience. This research leads toward a visual analytic system for multimedia analysis that can combine relationships in multimedia data with relationships in text. We have been identifying the features and entities necessary to exploit, extract, and learn the relationship patterns in multimedia content.

In FY 2012, we began developing a new multimedia software system for integrating and analyzing cyber data comprised of activity logs and the multimedia content it references. We made advances in two broad areas: the creation of a framework for synthesizing multimedia data, and the development of a visual approach for linking image relationships with textual relationships.

First, the creation of a multimedia relationship framework began with the identification of patterns within image and video data by applying classifiers that run during the processing of data. Classifiers are created first by detecting features and then training the system to recognize images with similar features. Each media type has a variety of features associated with the type. For images, we calculated several features, including dense scale invariant feature transform descriptors, pyramid histogram of gradient descriptors, and red–green–blue joint histograms. Once the features are identified, we “train” the system using a series of support vector machines – one for each feature type – using a pre-collected set of exemplar images. After training on the exemplars, the system combines the results of each classifier to produce a composite score, which determines whether an image belongs to a classification. For demonstration, we trained our system on classifiers to detect images of computer-aided design drawings, charts, circuit diagrams, washing machines, and refrigerators.

In addition to classification, we chose to identify patterns within image and video data by applying clustering methods after the feature identifications step. In this way, we can offer a general characterization of the image data in addition to the classification, which can become valuable when appropriate classifiers have not yet been trained. The scores from the classifiers and the cluster information are then stored along with text data gathered from the cyber log information in the relationship framework and fed to the visual interface.

We are working with subject matter experts to ensure that our advances will be applicable to cyber intelligence. We began the creation of a visual interface through a user inquiry analysis of six analysts that work with cyber intelligence at PNNL. From this inquiry, we determined that the users would benefit from a novel visualization that could reveal multidimensional relationships within multimedia. We chose to create a multimedia faceted search visualization. To date, faceted search visualizations have been used exclusively with text data. We extended this concept to image and video data providing a faceted search visualization for multimedia through the inclusion of image and video clustering and classifiers. The multimedia faceted search reveals co-occurrence relationships, and the faceted search tool allows the user to correlate between images that have matched certain classifiers and different columns from the log data, especially those query terms used to reference the multimedia content. In FY 2012, we created a fully operational system that includes both the relationship framework and the multimedia faceted search visualization.

We have deployed our prototype for use at PNNL and have modified the system based on user feedback. As part of the input received, we determined that the analysts often need novel tools for exploration of the relationships among multiple (often three) dimensions in their data. We have begun exploring additional visual metaphors that will aid in the analysis of the relationships among these dimensions. Thus for FY 2013, we will extend this concept into a new visualization that can graph actors and locations while adding supplementary dimensions based on similarity of multimedia content.

PN12050/2451

Multi-Resolution Data Model and Directed Data Reduction, Reconstruction and Aggregation

Kerstin Kleese van Dam

This project is delivering a collection of event and relationship descriptions and algorithms for identifying these phenomena across an archive of multi-channel historical data.

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 substations 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 on not only 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 will report on status and deliver operational information and act as receptors of information and instructions (i.e., reduce demand/production).

The original focus of this project was developing a multi-resolution model as a data transport framework for 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. The fundamental assumption underlying this work was that the amount of data generated by various sensors in the power grid (PMU data in particular) in the future would overwhelm communications systems, and this type of streaming re-prioritization of information would be required to ensure that the critical information was effectively communicated to the power engineers.

During the first year of our project, we quantified the amount of information that can realistically be expected from PMUs nationwide once the technology was fully deployed. Our best estimate is that there will be a maximum of 50k PMUs distributed across the nation when fully deployed. This leads to an aggregate national bandwidth requirement of 144MB/sec. Given current communications protocols (e.g., 10GigE, 802.11n) and trends, our analysis implies there will be no bandwidth issues in transporting the data generated by the PMUs. We published a conference paper outlining our conclusions.

During the second year of our project, we focused primarily on developing a better understanding of the generated data, particularly various types of events and translated that understanding into algorithms for use in detecting these events. We obtained access to approximately 1.5 years' worth of PMU data (2 TB) and identified several events of interest within this data set. Next, we performed an interactive analysis of the entire data set by using the R statistical package running over a Hadoop cluster, dynamically generated on the PNNL Institutional Computing (PIC) environment. By using over 415,000 hours of compute time on PIC, we characterized the underlying data by interactively testing hypothesis against the entire data set. This was critical because many of the events in which we were interested happen rarely, limiting the value of traditional techniques such as data sampling.

During FY 2012, we spent significant time developing several algorithms to identify erroneous data elements. These algorithms range from fairly straightforward data stream analysis (e.g., if the value remains constant for more than 10 min, there is a problem with the sensor) to much more complex analysis (e.g., comparing frequency trends across PMUs to identify when a sensor is not reporting correctly). Coded in R, these algorithms were applied against our entire data set and have been used to generate a "cleaned" data version in which all known PMU sensor errors were eliminated. We are using this new data set as the basis for identifying other events of interest, beginning with generator trips. An initial version of our generator trip identification algorithm has been created and the results of applying this algorithm across the historical data set are being reviewed by domain experts.

During the course of this project, we also developed a repository where we can record metadata about specific events for fast retrieval through either a SQL interface or a custom API. We designed an ontology capable of representing events in general and have used it as the basis for design of the relational database schema. This repository is populated with generator trip events identified by our algorithms. In addition, we created a custom Java API that allows applications to answer specific questions about generator trip events. While the standard SQL interface provides a generic query capability, our API provides a domain-specific query capability that eliminates the need for the calling application to understand our event

PN11054/2376

ontology. This API optimizes query performance by ensuring queries use the underlying indices appropriately. The infrastructure component of this project will be transitioned and integrated into a new project in FY 2013 and thus will not be an ongoing task for our current work.

Our initial algorithms have focused on basic statistical analysis of a single data stream – that of PMU frequency data. Our final year's work will expand on that foundation in two important ways. First, we will incorporate additional data streams (or modalities or channels). In particular, we will include other PMU channels in our analysis such as phase angle and external information such as weather. Once we have established this multi-channel data set, we will use it as the basis for significantly more advanced statistical analysis.

Our first step is to increase the number of data sets to which we have access. Currently, we are obtaining an update for our PMU data stream that will bring in an additional 2 TB of PMU data covering the past year. This data set alone will provide multiple channels for our analysis, including frequency, phase angle, and voltage. We are working on obtaining access to the WISP code, which generates a spectral analysis of sensor data. While this information is derived from PMU data, the resulting information provides a very different perspective of what is happening. We have been collecting weather data from several locations across the Pacific Northwest over the last year and will incorporate this information into our analysis. Additionally, we will work with AEP to obtain smart meter data from their distribution system that will provide a distinct sensor stream based on the grid's distribution network, allowing us to demonstrate the generality of our data analysis framework.

Once we have developed and validated a statistical model capable of detecting a specific event (such as bad data or a generator trip), an algorithm will need to be disseminated for use by other researchers. While the platforms for deploying analysis capabilities are being developed by other projects, we expect to work closely with these teams to ensure our models have a broad reach. This close collaboration is required because adapting an existing model for deployment involves a deep understanding of both the constraints of the deployment platform and the model itself.

In FY 2013, we will demonstrate the feasibility of transitioning our models to a distributed platform with limited computational resources by working with the Volttron™ team to deploy our data cleaning and generator trip detection models. We selected Volttron™ as our demonstration deployment method because it is a particularly challenging platform for data analysis. In Volttron™, a model is deployed as an agent on a device (e.g., a PMU or PDC) that has access only to information that passes through that specific device. As a result, any assumptions about access to external data or a global perspective must be removed from the model. Further, each device has limited resources and thus models must be modified to work on streaming data (e.g., by employing windowing techniques) and requires that the model work on only a specified amount of information in order to execute. Finally, the models must be enhanced to work in near-real time because information ineffectively processed information will be lost.

Multiscale Models for Microbial Communities

Haluk Resat

This project is developing mathematical models that incorporate the possible effects of a heterogeneous 3D structure, the functional biodiversity of the microbial population, and geochemical processes into a unified model to improve our understanding of the interactive roles between co-existing organisms in a microbial community.

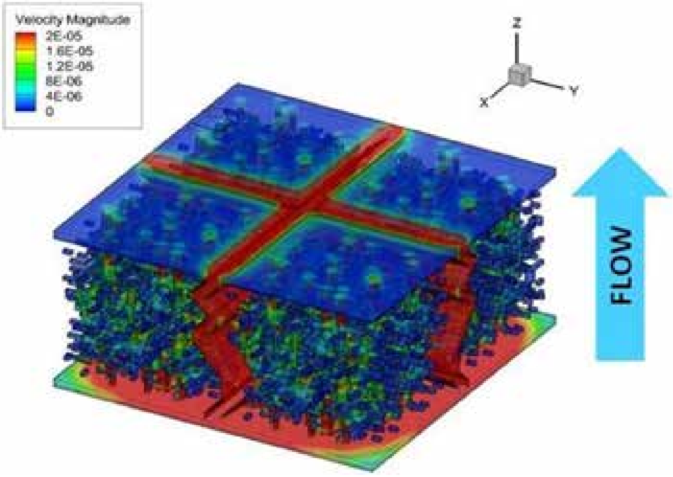
Soil is a highly complex heterogeneous system in terms of inhabitant microorganisms and spatial properties. Metabolic activity of microbial organisms is strongly coupled to the local environment conditions. At the microscale, variations in local environmental conditions cause microbes to encounter highly heterogeneous living conditions. Our aim is to develop mathematical models that incorporate the possible effects of the heterogeneous 3D structure, the 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 the microbial community-based management practices in controlling and regulating carbon flow in soils.

In the earlier phase of the project, we developed a metabolic network model for bacterial dynamics in soil microaggregates. We then used our model to predict which type of cellulose degradation mechanisms might give survival and growth advantage to bacterial organisms in the soil system. We observed that microbial types with different hydrolase enzyme expression strategies can have different functional niches in cellulose utilization. Our kinetic model made it possible to predict 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. Recently, we extended these studies to investigate how the carbon capture and utilization efficiency in soil aggregates depend on extracellular hydrolase production rates by microbes, diffusivity of the hydrolases, pore structure and aggregate packing, and insoluble carbon substrate distribution. A pursued sensitivity analysis predicted that the properties of the surrounding environment (i.e., aggregate packing) impact carbon acquisition and utilization by the bacteria more than the hydrolase enzyme production levels as well as the enzyme's biomolecular properties and diffusion constant. In the context of ecological systems, our results suggested that microbe-environment interactions must be considered when the interaction between different guilds (e.g., extracellular enzyme producers and cheaters) are investigated.

Preferential flow pathways determine how soluble nutrients would be carried around in the soil system. One open question is the partitioning of the flow through the inter- and intra-aggregate pores. We used computational fluid dynamics simulations to determine the flow patterns in aggregate-of-aggregates structures. Stacking the aggregates with varying distances between them allowed us to compute how the flow is partitioned between intra- and inter-aggregate flow pathways as a function of the spacing between the aggregates.

We found that the soluble factors are mainly transported via flows through inter-aggregate pores, and that the flow capacity through the aggregates is less than 2% when the spacing between the aggregates is larger than 18 μ. Such studies enable us to identify what kind of assumptions in the models are realistic and which computational methods are required to investigate the bacterial dynamics in terrestrial ecosystems.

We will continue to employ the developed models in predicting the impact of microbe-facilitated carbon cycling processes in terrestrial systems. We will be upscaling the constructed quantitative models to pore scales with the eventual goal of making them modules for earth system models developed by the wider scientific community. Such efforts are being actively pursued by the DOE Terrestrial Ecosystem Science and other BER program offices.



Flow patterns through the inter- and intra-aggregate pores in an aggregate of a four soil micro-aggregate construction that represents a small segment of the soil system. Spatial dependence of the flow rates is shown with a color map, where red and blue correspond with high and low flow rates, respectively.

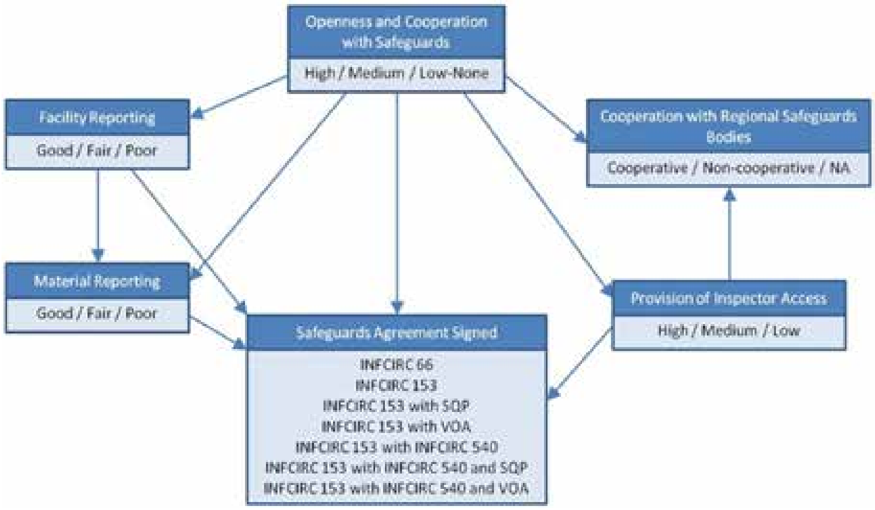
Multi-Source Signatures of Nuclear Programs

Paul D. Whitney

This project is developing, validating, and demonstrating contextual, model-based data signatures in a variety of nuclear intent analytic challenges. If successful, these signatures will enable identification of nuclearization features and support analysis of those features that are consistent with the informed intuition of nuclear proliferation subject matter experts.

Detecting and identifying the intent to develop or further a nuclear weapons program requires input from diverse sets of expertise, and requires understanding of diverse types of information and data. Currently, this analytic activity is executed by teams of analysts. While expertise typically crosses multiple disciplines, the entire set of required capabilities does not reside within any single analyst. This project addresses both the heterogeneities in data and expertise to develop normalized, context-informed, summaries of the data used to assess nuclear intent. These issues are addressed by representing analytic expertise and known relationships as influence diagrams or other modeling formalisms. The model-based approach codifies expertise and makes explicit various process models.

Through this project, we are demonstrating the signatures in the context of nuclear non-proliferation models and data. Our goals for FY 2012 were to commence developing the mathematical framework for structured analysis, assemble two examples with data to study the analytic process, and begin formulating various models based on the experts' knowledge.



Bayesian network model of a state's cooperation with international safeguards agreements.

Mathematical Framework. In FY 2012, this project developed the mathematical framework used for assessing nuclear facilities. Given a collection of expert-based mathematical models for evaluating features of nuclear facilities and a collection of possibly relevant data objects, the expert-based models are evaluated against the content of each data object. The model outputs are comparable across all data objects, thus normalizing different data types for comparison. Model outputs that are unusually distributed compared with the typical distribution across a row of features are selected as "topical;" these become the basis for features. Because the models carry the domain context, the resulting signatures based on those features can be mapped into the domain context. These numeric signatures can then be used for clustering, outlier detection, or comparing facilities.

Analytic Examples. The second goal for our project during FY 2012 was to facilitate the development of expert-based models by assembling two examples with data. Two examples were chosen: one case in which the outcome was known with a degree of confidence, and a second case where the outcome was uncertain. For each example a mix of source types was used (imagery, text, etc.). The analysts determined which of the many pieces of data were truly critical to the analysis. In the course of assembling the examples, the experts also developed a list of relevant facility attributes, and categorized each piece of critical data according to which attributes the data was relevant.

Expert-Based Models. The final goal for FY 2012 was to begin development of expert-based mathematical models, specifically Bayesian networks. The models fall into two broad categories: those based on the list of engineering attributes identified by the nuclear facility experts and those models based on human behavior and motivation modeling. The latter focused on political and social factors relevant to a state's decision to seek nuclear technology. Currently, there are five engineering and five human behavior models under development in various stages of validation.

In FY 2013, this project will develop a third example with associated data in order to ensure that all relevant information is considered in the mathematical models. In addition, the expert-based models currently under construction will be completed and validated. The finalized models can then be used to create the facility signatures.

PN12053/2454

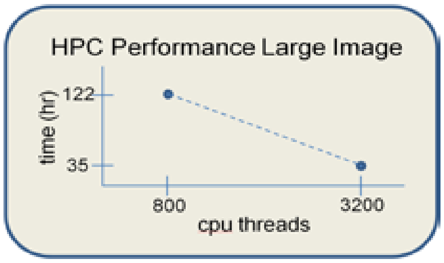
Nanoscale-Macroscale Three-Dimensional Integration Using High Performance Computing

James P. Carson

This work establishes the capability to generate 3D datasets of macroscale data at nanoscale resolution by collecting multiple serial 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.

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 associate nanoscale events rapidly into the context of the macroscale is essential to achieving greater innovation in research.

This research brings genes, macromolecules, and cells imaged at sub-micron spatial resolution into a 3D organ system context. 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 nm. These images can be computationally stacked into a volume representation at subcellular resolution.



Processor count scalability on the Cray XMT using parallelized image registration code.

Development of this capability is part of the emerging field of bioimage informatics. Although 2D 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 the University of Washington, we commenced production of serial sectioned multicellular pulmonary datasets. Each image in these test sets is approximately 80000 × 80000 pixels, which is equivalent to the image size produced by a 6400 megapixel camera. These datasets represent different embedding conditions, various sectioning distances, and two different organisms: a mouse and a rat. By acquiring datasets under these different variables, the effects of these variables on computational performance can be examined. Then, 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 time, 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 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 arrangement will allow features detected in the unaltered data to be properly translocated into the reconstructed dataset.

In FY 2012, we applied the registration and warp-smoothing techniques developed in FY 2011 to the high resolution

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mouse pulmonary dataset that was also acquired in FY 2011. Results suggest the pulmonary data is more challenging than the hepatic test dataset for image registration performed at the highest resolutions. This is likely due to the sparse nature of pulmonary tissue and the significant variation in shapes in sections 100 µm apart. This suggests improved quality can be achieved via decreasing the spacing between acquired tissue sections.

For FY 2013, this project will continue implementation of 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.

Next Generation Network Simulations for Power System Applications

Oreste Villa

We are developing a next-generation modeling tool that captures the interaction of communication technologies with the power grid. This enables power systems engineers to understand and address the challenges of communication quality of service on the control, monitoring, and operations of future power systems.

New smart grid technologies and concepts such as dynamic pricing, demand response, dynamic state estimation, or wide area monitoring, protection, and control are expected to require considerable communication resources. As the cost of retrofit is too high, future power grids will require the integration of high-speed, secure connections with legacy communication systems while still providing adequate system control and security. Considerable work has been performed previously to co-simulate the power domain with load models and market operations; however, limited work has been performed in integrating communications directly into a power domain solver.

We are developing a scalable, high performance simulation infrastructure for data communication networks for power transmission and distribution power grids. Our goal is to develop a unique infrastructure that will position PNNL as the leader in modeling and planning power grid data communication networks. This project will yield a general scalable high performance computing (HPC) communication network simulation, modeling, and planning infrastructure. We will investigate bottlenecks and limitations in state-of-the-art simulation infrastructures, proposing new approaches, parallelization methods, and high level algorithms to enhance performance. We will map and optimize existing simulations to state-of-the-art HPC computers, proposing new engines for integration with current simulation infrastructures. We will also interface existing power grid simulation infrastructures with the new proposed network simulation, identifying network properties and requirements representative of the power grid network domain.

For FY 2012, initial progress for a co-simulation environment for power and communication systems was created and tested using GridLAB-D and NS-3. An open-source Message Passing Interface (MPI) system was used to create a set of glue codes to synchronize time between the two simulators, pass information between the two simulators at given time intervals, and handle any error messaging or re-tries required during the simulation.

A test case was developed that focused on a transactive control strategy simulated representation of the real-time demand response program of the gridSMART® Demonstration project. It used two-way communication at 5-min intervals to communicate a device's state information and desire to consume electricity to the centralized auction device, and the actual value of electricity as determined by the auction back to the devices. The process required a robust communication system supporting hundreds to thousands of devices, and significant latency in the communication system can cause power system performance problems.

Balancing distributed simulations in NS-3 was also tested in FY 2012. We found that the time to serialize a node (the whole TCP/IP stack, routing table, and the applications) is a significant portion of the run time and hampers the performance. After reviewing the code, it was realized that the problem was because of the strong dependencies between objects in NS-3. We need to investigate the dependencies and convert some of the pointer references and remote references to optimize the de-/serialization operations. In fact, we have seen an instance of this problem in GridLAB-DI. Dependencies will cause major problems when we are porting parts of GridLAB-D and NS-3 to the new simulator engine and will be investigated in FY 2013.

Integrating communications into a domain solver for the simulation of communication and power systems to form an interrelationship. Communication system latency, cyber security, and topology all will affect the power system itself and the controls to operate the power system.

PN12054/2455

Increasing modularity will also allow us to build an efficient roll back mechanism. With such a mechanism, we can increase the fault tolerance of both simulators and provide optimistic synchronization for integrated simulation. Currently, we are using pessimistic scheduling for synchronization: we keep simulators waiting for each other to keep the global time in sync. However, we only need to ensure synchronization when one simulator needs to send a message to the other. Optimistic scheduling is developed to achieve this: it does not try to keep times in sync and instead ensures that the times are synchronized only during message exchanges. During message exchange, it also rolls backs the simulators to the same time and restarts the simulation. Optimistic scheduling relies heavily on efficient roll back, which needs modular software. In FY 2013, we will investigate whether optimistic scheduling can be applied to reduce simulation time for integrated models.

Also during FY 2012, we developed an HPC-oriented simulation engine for network and systems. The Next Generation Network and Power Simulator (NGNPS) is a parallel and distributed object-oriented code used to simulate the time behavior of systems composed of various components that update their state and communicate to each other. For instance, NGNPS can be used to simulate computer or communication networks, supercomputers, power grid networks, agent based systems, and generally any complex system that can be modeled as a set of components that update their status every variable time step and exchange messages. NGNPS is parallel across a machine composed of multiple nodes (cluster) by using MPI and parallel within each node that composes the machine using pthreads. Components are virtual classes that need to be specialized to implement the behavior of specific entities in time. The typical component updates its state following states in a state-machine. The user of the engine has to define the time behavior of components for the system interested for simulating. Specialized components must be compatible with NGNPS interfacing APIs, and they can be compiled as a stand-alone library and loaded at run-time by the engine. This allows designers of components to distribute only objects of their implementation without releasing the source code.

Components can be different entities in a power grid network and in a communication network. In this context, we envision a repository of different components libraries representing the time-series behavior of the energy consumption of electric vehicles or houses, and the routers and networks used to collect this information. System topology (i.e., connections among components) and attributes for different components can be specified in a configuration file loaded at start time by the simulation engine. NGNPS assigns simulated components to computing elements by distributing equal amount of workload to different nodes in the cluster and minimizing communication among components. This information is extracted from the topology file used to initialize the simulation.

In an object-oriented distributed simulation infrastructure such as NGNPS, serialization and deserialization functions are used to provide:

- an infrastructure to partition and distribute the simulated model across a cluster, allocating a portion of simulated components on the various physical nodes of the cluster.
- a low-level communication infrastructure that collects and aggregate messages exchanged between components allocated on different physical nodes in the cluster.
- a mechanism for fault tolerance by providing capabilities to checkpoint and restart the overall simulation by saving and restoring the state of the components on disk.
- a load balancing scheme that (at run-time) migrates components from one physical node in the cluster to another, destroying and resurrecting them as necessary to maximize overall performance.

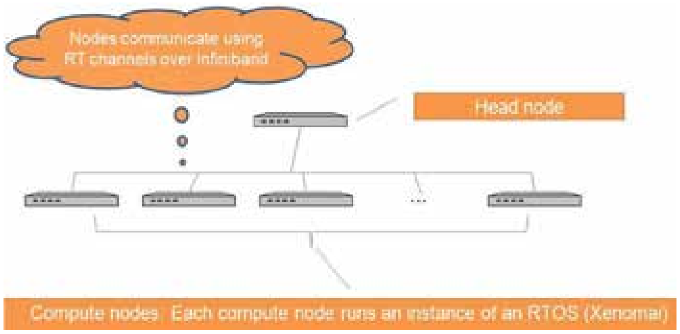
While the NGNPS engine can call de-/serialization functions for the virtual class component, the actual code needs to be implemented by the user that designs the simulated system for each specific entity. To simplify this step, NGNPS relies on a compiler-based approach called Ser++ to transparently generate serialization and de-/serialization code for components. NGNPS is written in C++ and it is composed of approximately 3000 lines of code distributed over 20 classes while the Ser++ framework accounts for ~2000 lines of C++ code distributed across 15 classes. Both pieces of software were developed during the first year of the project.

FY 2013 will focus on integrating a transmission level solver, namely PowerWorld, into the co-simulation framework, exchanging information between the three simulators to form a single, cohesive simulation environment. This will accomplish several goals towards creating a more generic set of integration glue codes: 1) create a glue code set to allow information access and exchange with a commercial software package where source code may not be available and modifications cannot be made to the software; 2) synchronize simulation time across multiple domain solution methodologies (i.e., time is handled differently in a power system tool vs. a power system simulator vs. communication simulator); and 3) dynamically reassign time scales during an ongoing simulation (i.e., switching from steady-state, time-series analysis to transient-based analysis when an appropriate event occurs). External users (e.g., Lawrence Berkeley National Laboratory, University of Washington, National Institute of Standards and Technology) have expressed interest in using our collaborative development of the integrated system for business case scenarios and testing communication requirements with smart grid investments.

Real-time High-Performance Computing Infrastructure for Next-Generation Power Grid Analysis

Peter S.Y. Hui

We are developing a platform for real-time computation in a high-performance computing (HPC) 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.



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.

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, 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 in size and complexity. With streaming sensor data in the grid potentially reaching rates on the order of terabytes per day, analyzing this data subject to real-time guarantees is daunting and will require an HPC capable of functioning under real-time constraints.

We spent FY 2011 building the infrastructure foundation. We scoped the requirements for a small-cluster computer and purchased one Infiniband switch and one Ethernet switch. We developed a traffic prioritization for the Infiniband hardware interconnect that would enable higher priority traffic to be transmitted with higher precedence than low-priority traffic. For a real-time operating system (RTOS) to be deployed on each of the compute nodes, we evaluated several candidate operating systems, which led us to choose Xenomai with its support for hard real-time deadlines; its simple, clean, "user friendly" API; and its wide and active user community. Finally, we prepared to integrate the software stack and sample power grid kernels into the RTOS real-time kernel.

For FY 2012, our focus was developing a real-time version of a power grid analysis routine, specifically an application for dynamically estimating the electromechanical states of the power grid. Briefly, the chosen application targets one of the goals in simulation-based modeling of a power grid network to assess conditions, such as network stability at a given time. The application models the network using a system of mathematical equations for the states of the network, and then solves these equations using an ensemble Kalmann filter. To keep up with the rate of data generated by the Phasor Measurement Units deployed on the power grid, the goal of the system is to be able to compute results within 30ms.

We developed a method of formally verifying the code to run within the stated time constraints, something that has not previously been done in a parallel environment such as ours. One of the challenges was capturing complex timing interactions that occur in a parallel computing environment and guaranteeing that with all of the various possible control flow paths among the processes and with complex fork/join interactions between them, all timing requirements could still be met. We took the approach of first modeling the control flow of each of the parallel processes using timed finite automata, specifically including points at which child processes were spawned and joined. Next, we analyzed control flow automata to determine the worst case execution time of all component processes. We also examined the model for possible interactions between the processes. Combining this analysis with worst-case delays, we determined that timing constraints on the system would not be violated. By scheduling all processes with Xenomai, a Linux-based real-time operating system, we implemented a time-bounded matrix multiplication kernel which is capable of provably processing 128 × 128 matrices in under 9ms/cycle, well within the 30ms delay goal.

We presented a paper and poster at an international symposium and have submitted two additional conference papers. For these potential presentations, we described methods used to verify time-critical temporal constraints in a parallel environment and our efforts to develop a real-time dynamic state estimation application for the power grid.

PN11065/2387

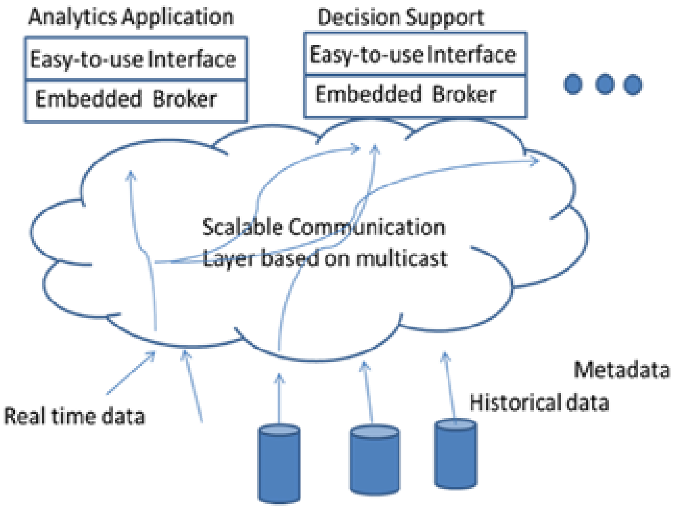
Scalable Sensor Data Management Middleware

Jian Yin

> ***This project is motivated by the explosive growth of power grid system sensors and an increasing number of innovative analysis applications that can use sensor data to improve operation efficiency and increase power system reliability.***

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.



The data fabric of the power grid software integration framework.

PN11066/2388

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 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. We also 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 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 achieved several orders of magnitude performance improvements over traditional systems. Performance is also predictable and consistent, which is crucial for real-time data ingestion. 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 leveraged solid-state devices and implemented a distributable version of our system that can use parallelism and improve performance. Building on this fundamental building block, we designed and prototyped the data fabric of a scalable and flexible data management middleware to mediate the enormous amount of data from a large number of sensors and a large number of applications in future smart grids. This data fabric becomes the core part of the PNNL-developed GridOPTICS, a novel software framework for integrating a collection of software tools into a coherent, powerful operations and planning tool for the power grid of the future. This framework enables plug-and-play of various analysis, modeling and visualization software tools to improve the efficiency and reliability of power grid.

To bridge the data access for different control purposes, we provide a scalable, lightweight event processing layer that hides the complexity of data collection, storage, delivery and management. The main challenge is the requirements to access huge amount of real time data. We address this challenge though scalable system architecture that balances system performance and ease of integration. While high-level data and communication software layers make integration easier, indirection causes high overhead and unpredictable performance. We designed our system to be as close to hardware as possible and still provide a thin and light weighted layer to allow easy integration of a diverse set of applications.

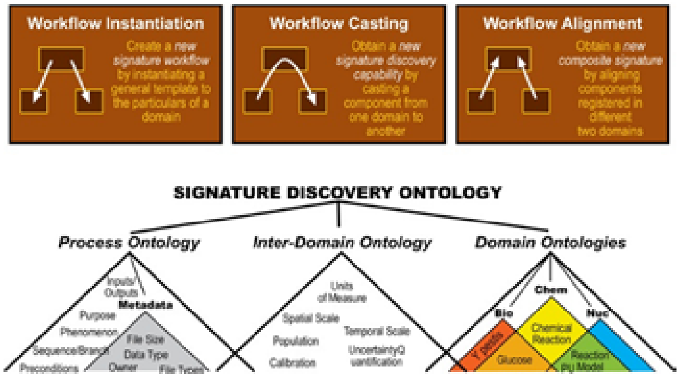
The detailed system architecture is shown in the figure. We applied our framework in integrating several power grid analytics and visualization applications and the initial prototype of GridOPTICS was demonstrated with several use cases. Empirical studies and experimental results shows that our system 1) provides essential system building blocks to enable future power grid applications; 2) provides the essential real time data fabric for GridOPTICS; 3) achieves real-time predictable performance for data access; 4) performs close to the hardware limit; 5) offers linear scalability to multiple nodes; and 6) allows easy integration of a large number of diverse power grid applications that requires reliable, efficient, real-time access of power grid data.

In FY 2013, we will build on the previous work and continue to improve the performance of our systems. We will also investigate the reliability and fault tolerance design of our middleware. Finally, we will design and prototype system mechanisms to improve system reliability through replication and adaptive reconfiguration.

Semantic Workflows for Signature Discovery

Cliff A. Joslyn

We seek to generalize signature methods across domains by providing a semantic layer to the Analytic Framework (AF). Equipping workflow components and data items with semantic type specifications representing the type and content of information flows allows measurement of similarities and recommendations about interoperable methods and algorithms.



Workflow and ontology relationships and processes.

This project develops methods, measures, and algorithms to guide scientists and researchers to automate construction of signature discovery workflows and identify new composite signatures. A workflow to serve one domain (bioforensics or biomarker discovery) may have individual analytic components, portions of analytic workflows, or entire analytic workflows useful in another domain (e.g., chemical forensics or insider threat discovery, respectively). We will identify these similarities in workflows and/or their components; provide software services to the AF to provide capabilities to reveal these to users and provide means for them to exploit opportunities for re-use of existing components and workflows with perhaps some modification. Most importantly, we will support the capability to discover opportunities for re-use and integration of signature workflows and their components that are not apparent at first observation.

Focus Selection. Developing semantic technologies targeting a broad area of applicability like signature science requires a phased approach. Initially, we provide a focused, domain-specific demonstration in the context of development sufficient to demonstrate applicability and feasibility. We sought to instantiate and demonstrate the value of semantic technologies by selecting the domain of cyber-sequence analysis, interacting closely with the Data-Intensive Algorithms for Bioinformatics-Inspired Signal Detection (DIA) project that integrates with AF demos and provide coherence while focusing on qualitative, symbolic data while remaining generalizability to biological analysis. The initial determination is whether sequences representing signatures discovered in test program executables are semantically compatible with sequences representing entire specific executable programs by providing semantic annotations of arbitrary sequence files as a Boolean match/mismatch. Subsequent goals are to support users in selecting from a palette of potential sequence or profile detectors, measuring quantitatively the most semantically similar components.

Semantic Services for AF Middleware. We provided the ability to equip software services as AF workflow components with semantic metadata, including semantic annotations of component ports and data items in the AF Library through SAWSDL protocol. User roles (Component Developer, Component Annotator, and Workflow Creator) interact with the AF Library and SDI Knowledgebase (semantic triplestore) to register the semantics of component ports and measure similarity. This allows Boolean and quantitative type-matching at workflow construction and execution times.

Semantic Content Development for Signature Discovery. Identifying, integrating, and developing needed semantic resources requires lexical (terminological) and ontological (conceptual) development. We integrated terms from other project use cases with internally and externally developed ontologies from signature science, cyber, and knowledge system communities. Relying on Basic Formal (U Buffalo) as a top ontology, we are exploiting the Sequence, Information Artifact (U Buffalo), and our own Semwork ontology at the inter-domain level. At the signature-generic level, our Signature Discovery and the Ontology for Biomedical Investigations (U Buffalo) will interact with cyber domain ontologies acquired from academic and government communities (UMBC, U Buffalo, Mitre). We are outreaching to sponsors and agencies for collaboration and further development.

Comparing Semantic Annotations. Quantitative annotation comparison requires development, implementation, and testing of analytical methods to measure similarities of workflows, components, and data items, in the context of user-cases for recommendation of data and component generalization and selection. We advanced our mathematical methods for metrics in ordered sets for measuring distances between concepts and sizes of regions circumscribed by groups of concepts in semantic hierarchies.

Future work includes explication of a Hausdorf measure for measuring overlaps between multiple groups of concepts.

PN12070/2471

Signature Discovery Analytic Framework

Adam S. Wynne

Next-generation signature detection capabilities require 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 creates a software architecture that integrates novel and existing data analysis algorithms into a single, enterprise-strength 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 the high-performance computing resources 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 creating 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 FY 2012, we worked toward the above objective by creating a service-oriented design and comprehensive vision for the analytic framework consisting of the following high-level elements:

Signature Discovery Workbench. This will be an innovative desktop application supporting both novice and experienced users that leads the user through the signature discovery process and recommends computational services and workflows to complete the user's stated task.

Analytic Components. These are the algorithms that implement the various signature discovery tools, which are made available to client applications via the Signature Analytics API as web services.

Signature Discovery Library. This is a database with an associated API that stores workflow templates, components, and data associated with signature discovery experiments. The other components draw on this information to measure the similarity between services, make connections between domains, and make recommendations to users.

Knowledge and Recommendation Engines. These contain the signature discovery knowledge base and assist the user in choosing and building workflows as the user proceeds through the signature discovery process.

We implemented, delivered, and demonstrated a set of integrated tools enabled by algorithms developed on the initiative throughout the year. The demonstration and testing of these tools focused on scenarios that illustrate common signature discovery tasks. These capabilities consist of 10 web services and 5 workflows covering 11 separate tools delivered by individual projects. The workflows retrieve input files from the library and store intermediate and final results back to the library. In addition, we extended the Taverna workflow environment by creating a plugin that allows a user to upload files to (and download files from) the library that are used as input to workflows. Specifically, the tools implemented were integrated into workflows to support the following scenarios:

- comparing the quality of an existing signature for detecting a threat chemical against a signature for the same phenomenon produced by a sparse representation signature
- comparing the accuracy of signatures to detect a set of land types using satellite imagery data
- using an alignment algorithm from bioinformatics to identify related executable files of interest.

In FY 2013, we will continue to work with other project teams to encapsulate their algorithms and tools as components that are available to other users. The work will be led by the individual projects and supported and guided by analytic framework team members.

PN11067/2389

Signature Quality Metrics

Landon H. Sego

Signatures that detect, predict, or characterize 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 ultimate 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 comment attributed to Lord Kelvin: "If you cannot measure it, you cannot improve it."

Components of the SQM methodology.

The goal of SQM is to provide researchers, developers, and decision makers with a holistic approach for assessing the quality of a signature systems as they move through the stages of research and development, construction and evaluation of prototypes, and eventual deployment in an operational environment. 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 has been to assemble a team of experts with diverse backgrounds, including statistics, economics, psychology, operations research, risk analysis, computer science, and decision science. Drawing on this diversity of perspectives, we developed a systematic approach for measuring signature quality. We are demonstrating the methodology in the context of actual signature discovery efforts. We explain SQM in terms of four components:

Fidelity refers to how well the signature system detects, predicts, or characterizes the phenomenon of interest. This includes metrics like sensitivity, specificity, accuracy, ROC curves, F-score, and the like.

Cost refers to resources expended to develop, deploy, and/or utilize the signature system. Examples include the cost of detection systems, the cost of consumable reagents, and associated labor costs.

Risk refers to the likelihood and consequences associated with decision errors that may result by employing the detection system. This helps investigators assess the tradeoff between false positives and false negatives.

Domain specific attributes (DSA) include any other factors which may distinguish one signature system from another that are not already accounted for by fidelity, cost, or risk. Examples of DSA include time-to-decision, system portability, human safety, ease of use, and the like.

SQM also includes techniques to aggregate all the relevant metrics into a single decision framework that can be used to compare various alternatives using decision theory. The outcome of the SQM project is a set of metrics that may be used to assess and visualize the quality of a signature detection process in any domain.

We have nearly completed the application of SQM to three areas: 1) gamma-ray PVT sensors for radiation portal monitoring; 2) bioforensics analyses of *Bacillus anthracis* or *Yersinia pestis* dissemination; and 3) peptide identification, an essential component of proteomics.

Our research plan for FY 2013 has three components. First, we plan to conduct theoretical investigations to advance the state-of-the-art in assessing signature quality. Second, we will continue to demonstrate and refine SQM in the context of application areas, especially to support other projects. Finally, we will continue to develop the software tools that will guide researchers in applying SQM to their own projects.

PN11068/2390

Single Node Optimizations for Extreme Scale Systems

Daniel G. Chavarría-Miranda

This project investigates the necessary design and implementation techniques to support efficient utilization of node resources for extreme scale scientific applications. We believe that the efficient use of node memory and processing elements are principal factors to achieve the levels of scaling and performance required for exascale applications.

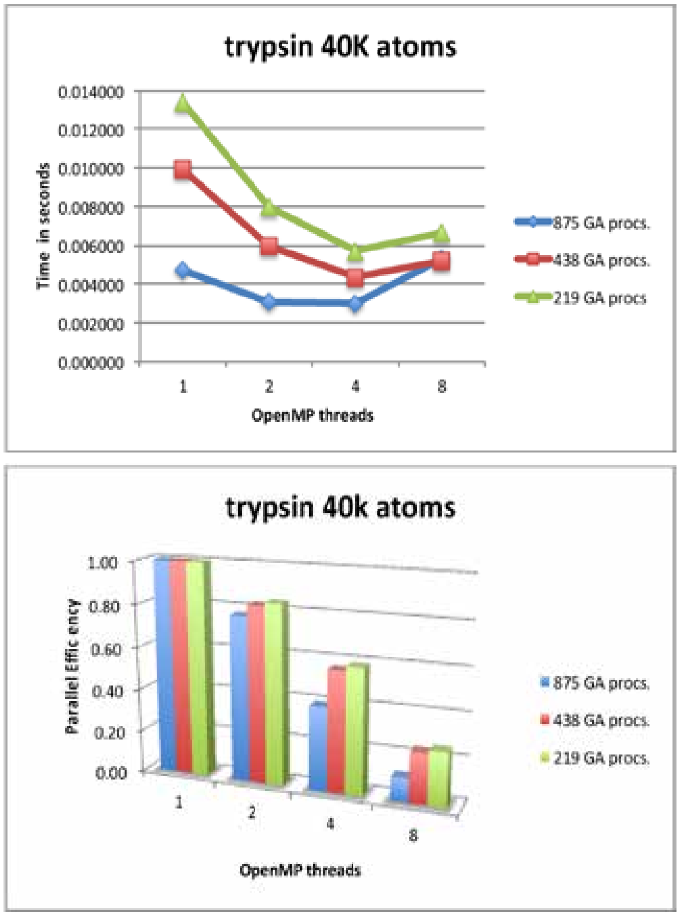
Extreme scale systems provide an unprecedented opportunity for scientists to attack larger, more complex problems and reach solutions dramatically faster. These new architectures promise to be qualitatively different from existing computers, and extracting their full capabilities requires significant 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.

Project outcomes include development of new optimization 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 2012, we focused on three primary activities: development and performance analysis of multithreaded kernels for the force calculations in the ARGOS classical molecular dynamics application and the performance evaluation of schemes to reduce metadata overhead.

We implemented a full set of multithreaded routines for the force calculation in 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. These routines have three versions for different interactions between molecules – solvent-solvent, solute-solute and solvent-solute – for a total of six multithreaded routines. Preliminary results show that OpenMP implementation is scaling fairly



Execution time per MD step and parallel efficiency for the multithreaded force calculation in the ARGOS MD package.

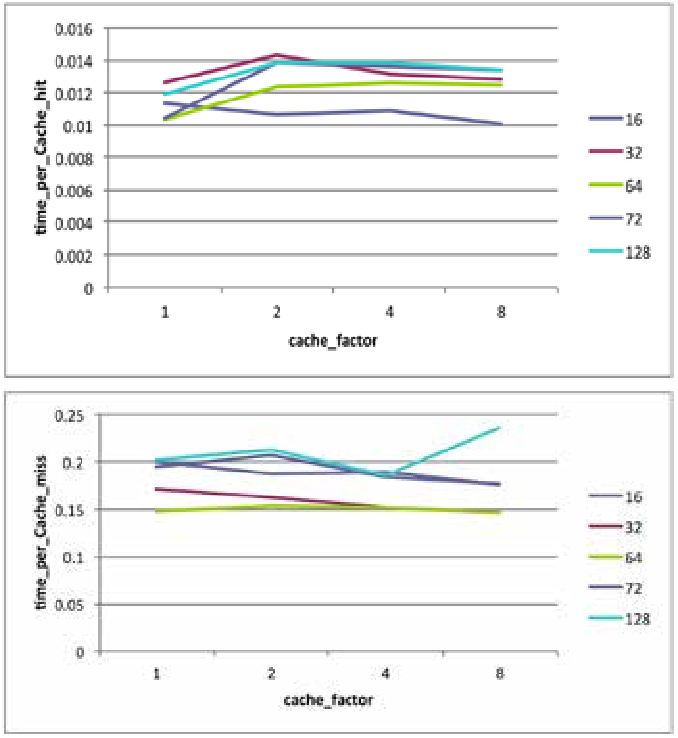
PN11069/2391

well as we increase core numbers. However, there is some overhead from the OpenMP parallelization for small input decks when we get to configurations in which each GA process owns just one or two cells. This is expected, as the amount of parallel work is small compared to the overhead of managing the parallelism. Our experiments were conducted on the PNNL institutional computing cluster (PIC), which uses AMD Interlagos processors, making the mapping of threads and processes to cores highly performance sensitive due to the non-uniformity of the memory system on the node, as well as the resources shared by every pair of cores. On this system, we map each GA process to a NUMA domain (four domains per node) and enable it to use all the cores attached to that domain (eight cores per domain). OpenMP threads are mapped on every other core except for configurations with more than four threads.

The execution time per MD step for a system of Trypsin molecules in water has a total of 40,000 atoms. The time is presented for an increasing number of OpenMP threads per GA process with an increasing number of GA processes as well. Parallel efficiency of the OpenMP execution is also presented. It is observed that as the number of GA processes increases (smaller number of cell-cell interactions per process), performance boost that is obtained from multithreading diminishes for this relatively small input deck. We also designed and implemented a framework to evaluate different metadata management strategies from full replication of metadata on every process to fully distributed metadata, which must be "remotely" queried on every communication operation.

Our framework incorporates the notion of "metadata servers," which essentially would be processes dedicated to storing and serving metadata on demand to the compute processes. Metadata servers would not participate in the application's computation and would instead dedicate their memory and processing resources (cores) to attend to metadata requests from compute processes. On the other hand, the compute processes can better manage their memory resources to maximize available memory for the application's data structures and minimize memory used in infrastructure support. We enable compute processes to use a configurable LRU cache that can vary in size depending on the application's needs. In this manner, the space dedicated to metadata use can be proportional to a fixed constant (O(1)) rather than proportional to the number of total processes in the job (millions of processes for exascale systems).

We used a communication trace of the two-electron calculation of the SCF application described last year and mapped its use of GA instance metadata. The experiment uses a logarithmic number of dedicated metadata servers (4 to 7) to attend an increasing number of compute processes (16 to 128 processes, one process per node). The plots present the average time in milliseconds per cache hit and cache miss for different cache sizes ranging from proportional to the total number of processes to 1/8 of it. As can be observed from the plots, the cost of cache hits is quite small and the cost of cache misses is proportional only to the cost of the remote network transfer, thus indicating the effectiveness of a metadata caching mechanism.



Metadata query cost with LRU cache and distributed servers.

In FY 2013, 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.

PN11069/2391

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 hot 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 marketplace 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.

During both FY 2011 and FY 2012, we identified several gaps and have enhanced our design accordingly. Specifically, we pioneered a biologically inspired active component architecture that is composable, online programmable, and intrinsically resilient. We developed the bio-inspired cell-oriented architecture (COA), which is the foundation of the SoftShuffle that is being incorporated in our cooperative autonomic resilient defense platform for cyber-physical systems, built a demo of the COA engine, and integrated it with our automated recovery subsystem in a unified architecture. We have also successfully evalauted behavior non-determinism and developed a novel approach to measuring the amount of confusion and diffusion in the system at any time. As a result of this project during this past FY, we have presented and published four peer-reviewed papers.

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.

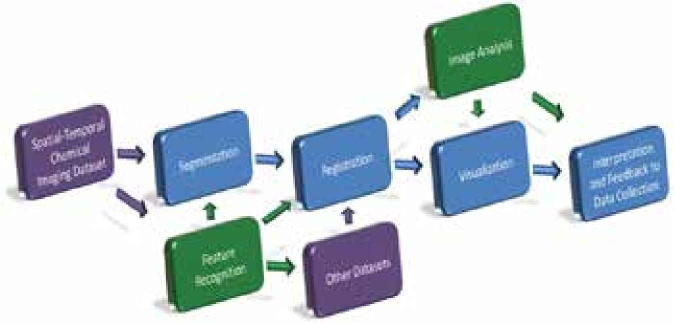
To make sure that our system is fully prepared, we have continually conducted rigorous evaluations.

PN11071/2393

Synergistic Integration of Feature Recognition and Analysis for Chemical Imaging Data

James P. Carson

This project is building the foundation for new and unique critical research capabilities 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 interactive role of feature recognition and image analysis on the multimodal integration framework for chemical imaging analysis.

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, which will allow 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 other projects, including 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 second effort investigated 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 quickly. Adjustments to the experiment can be implemented while access to the instrument is still available but only if necessary adjustments are noted. 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 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 was refined to increase both the utility of the toolkit and the capability for chemical imaging research. We additionally incorporated new objectives in the field of heterogeneous catalysis analysis. This work developed a test based on features stored in a quality database that determined if catalysis image data are unsuitable for analysis.

In FY 2013, the feature recognition toolkit will be adapted to the task of detecting nanomaterial and nanomaterial effects within living cells. The input and output of the toolkit will be integrated into a common image handling framework for managing chemical imaging data. 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.

PN11074/2396

Targeting Extreme Scale Computational Challenges with Heterogeneous Systems

Oreste Villa

Future high performance computing (HPC) systems are expected to integrate heterogeneous processing elements, such as GPU together with 86 conventional multicore processors. With this level of complexity, it becomes paramount to develop strategies and approaches to target these platforms efficiently.

Under this project, we are studying techniques and methodologies to support scientific applications on large-scale heterogeneous system. Our objective is to develop approaches, techniques, and methodologies (in form of software libraries or prototypes) to facilitate scientific application mapping on large-scale heterogeneous machines. Challenges associated with the use of these systems involve the refactoring of commodity applications to support new hardware features. New hardware features are dictated by evolution in architecture design necessary to achieve higher performance (shorter simulation times or larger simulations) or reduce power consumption. This project is an important cornerstone in understanding benefits and applicability of new computer architecture for applications of strategic importance such as molecular science, classical and quantum chemistry. The methodologies and techniques that are developed by this project will allow the next generation of molecular science, classic, and quantum chemistry applications to run efficiently on next generation large-scale heterogeneous systems. We are studying for instance code generators to allow for the easy porting of applications on new hardware (from high level description manageable by domain scientists), software layers to support transparent maximization of performance, and a reduction of power consumption.

A few highlights from project progress and accomplishments achieved during FY 2012 are described below.

Domain-specific code. We developed and implemented a domain specific code generator and auto-tuners for tensor contractions in NWChem to target a variety of architectures. The code generator is able to automatically generate code for GPUs with CUDA, OpenCL (AMD, NVIDIA), multicores with OpenCL, OpenMP, standard C/Fortran, and DGEMM + Sort. The code generator supports many options (such as the use of fused indices, streaming to overlap with memory transfers, use CPU to support GPU, etc.). Different versions and devices have different performance tradeoffs based on the type of input used. We have implemented runtime auto-tuning strategies based on heuristic and table to select the most efficient (in performance and power) options and methods for specific index range values and orders in contraction. We have demonstrated up to 8 times performance improvement respect to use conventional approaches.

Module designs. We have designed a generalized chemistry reaction module to be included in subsurface codes, climate modeling codes and carbon sequestration codes. We designed a C code version of the chemistry module easily parallelizable with OpenMP. When integrated on STOMP, it provides a 40% speedup (executed with the same amount of processing elements). Numerical accuracy is virtually unchanged. We are developing a CUDA version of the chemistry module to run on NVIDIA GPUs. We are also designing a hybrid version of it that will perform chemistry reactions where resources are available trying to maximize utilizations. Early tests demonstrate up to 12 times of potential performance improvement.

Transformation development. We are developing compiler- and auto tuning-based code transformations techniques for GPU. Modern GPU perform less efficiently if blocks of 32 CUDA threads (warp) follow a different control flow in the code execution. Also, if memory access patterns for the warp are non-consecutive within 128 bytes, performance is significantly reduced. This is usually referred as non-coalescing memory accesses and thread divergence. Following this consideration, we are focusing on loop transformations and iteration reordering to reduce memory access and threads execution irregularities. This is done by a combination of profiling, input characterization, and sampling. Early experiments demonstrate a potential of 35% of performance improvements when using loop transformation techniques. We envision a runtime layer that automatically recognizes input sets, which will enable the method to perform reordering of iterations based on machine-learning approaches.

Finally, we are targeting the execution of the ParaFLOW application on GPUs by using a set of custom codes developed on CUDA as well as a library-based approach by using Stencil++.

For FY 2013, we anticipate the completion of our CUDA chemistry modules and will continue working on runtime code transformation and iteration reordering for GPU. We are also planning to use the tensor contraction engine for GPU on multi-reference coupled cluster problem.

PN12074/2475

TASCEL: An Execution Model for Task-Based Optimizations

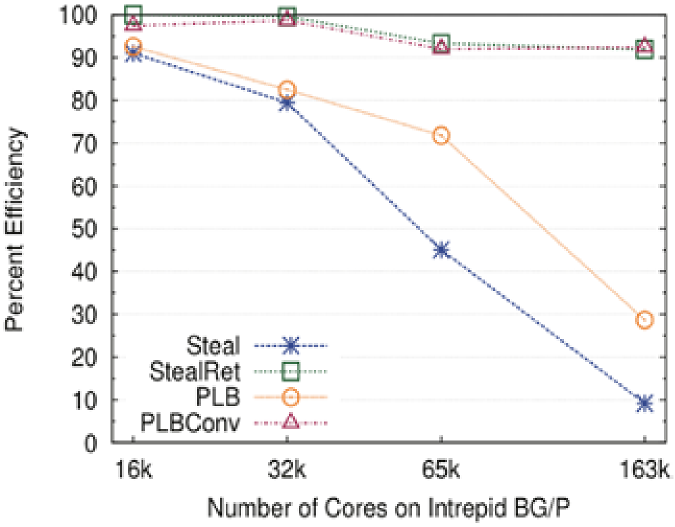
Sriram Krishnamoorthy

> ***We are developing a task-based execution model that exposes a higher level interface to programmers with a runtime that manages automatically the scheduling of computation and communication to optimize various metrics.***

Increased scale and variability in extreme scale computing systems makes it challenging to manage them effectively. This project focuses on developing task-based algorithms for distributed memory systems. While several specific instances of this model have been studied previously, we will design a runtime that incorporates key elements of prior approaches with focus on the design of scalable algorithms suitable for extreme scale platforms. The runtime manages the scheduling of the computation and communication to optimize various metrics (power, performance). Developed algorithms will handle various use cases for data access characteristics, computation granularity, communication requirements, and anticipated regularity. Algorithms will also optimize key computational chemistry methods and be released as part of the TASCEL library for use by the wider scientific community, enabling the development of performance portable applications for adaptation to underlying architecture with selective localized changes to the application through careful choice of algorithms and optimizations. The result will be sustainable software for effective porting to future supercomputing platforms with reasonable effort.

We developed a thread-safe active message-based framework for the design and development of task-based applications. Thread-safety enables natural sharing of data in a many-core system. Given the anticipated increase in core counts on future systems, thread-safety prepares applications for effective execution on future extreme scale systems. The active message framework enables efficient execution of complex transactions that could involve multiple round-trips using remote memory access protocols. The multi-threaded framework supports flexible progress guarantees for active messages, enabling the development of concurrent observer computations. Such computations act as sub-programs running concurrent with the application, observing and reacting to application and hardware actions.

Applications often involve iterative execution of identical or slowly evolving calculations. Such applications require incremental rebalancing to improve load balance across iterations. We investigated the design and evaluation of two distinct approaches to address this challenge: persistence-based load balancing and work stealing. The work performed is overdecomposed into tasks, enabling automatic rebalancing by the runtime. We developed a hierarchical persistence-based rebalancing algorithm that performs localized incremental rebalancing. We also present an active-message-based retentive work stealing algorithm optimized for iterative applications on distributed memory machines. We demonstrated low overheads and high efficiencies on the full NERSC Hopper (146,400 cores) and ALCF Intrepid systems (163,840 cores), and up to 128,000 cores on OLCF Titan. This work is published in the 2012 International Symposium on High Performance Distributed Computing.



Comparison of applications that improve load balance.

We employed the dynamic load balancing infrastructure in TASCEL to address homology detection, a fundamental problem in large-scale sequence analysis with numerous applications. We developed a scalable framework to conduct large-scale optimal homology detection on massively parallel supercomputing platforms. Our approach employs distributed memory work stealing to parallelize optimal pairwise alignment computation tasks effectively. Results on 120,000 cores of the Hopper Cray XE6 supercomputer demonstrate strong scaling and up to 2.42×10^7 optimal pairwise sequence alignments computed per second, the highest reported in the literature. An initial description of this approach to scalable homology detection has been accepted for publication in the 2012 Workshop on Parallel Algorithms and Software for Analysis of Massive Graphs.

In FY 2013, we will extend the TASCEL infrastructure to support data-placement awareness in terms of data locality and NUMA. The infrastructure will be extended to support efficient management of inter-task dependences. We will also implement a preliminary version of the complete iterative Coupled Cluster Singles and Doubles method.

PN12075/2476

Visualizing Uncertainty in Conceptual and Numerical Models for Geological Sequestration

Luke J. Gosink

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. Ultimately, this work will enable 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.

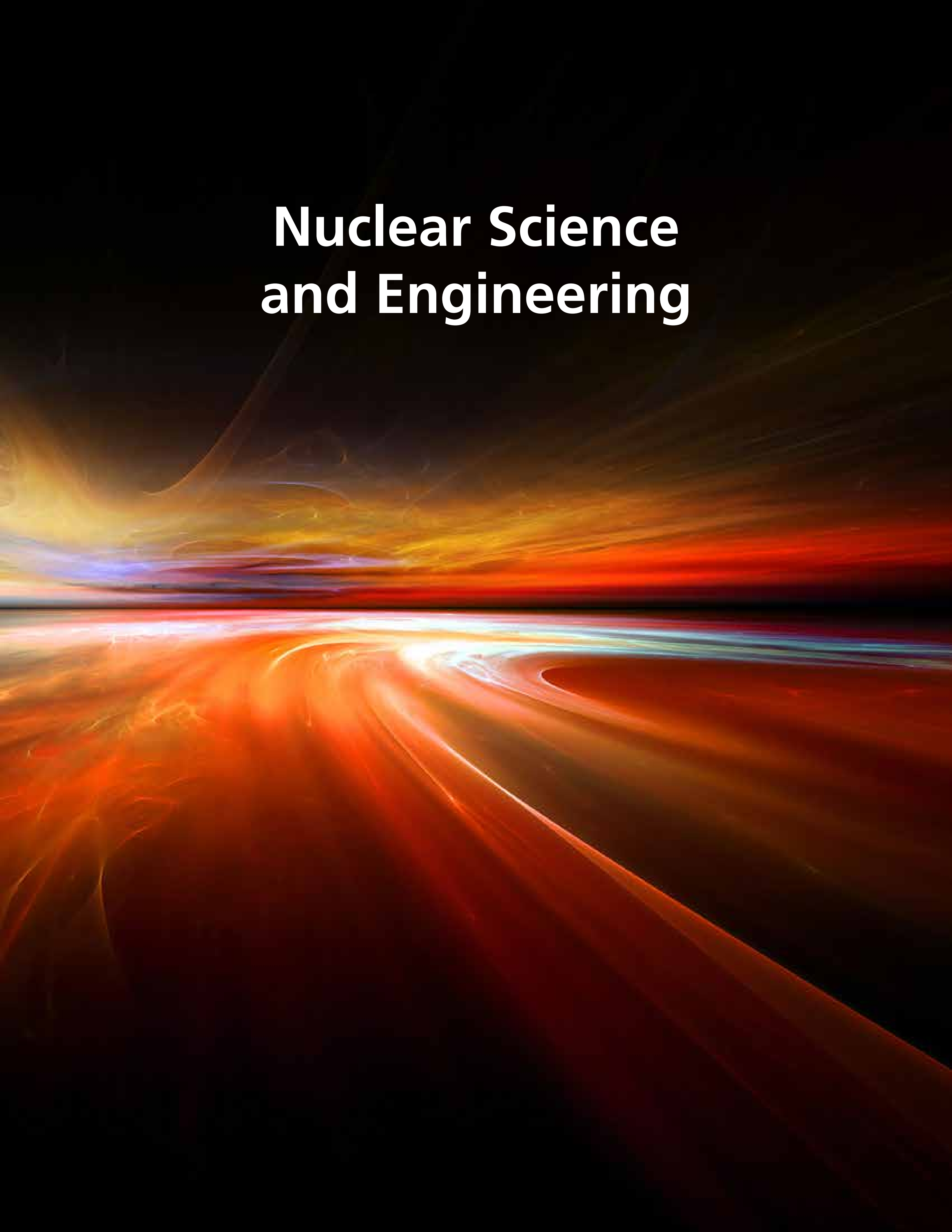
In FY 2011, we completed the construction of our statistical analysis framework for performing UQ. This framework is based on a Bayesian approach called Bayesian Model Aggregation (BMA) that combines ground truth observations (i.e., monitoring data) with the predictions obtained through an ensemble of 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. We 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 completed validation studies on our statistical framework. Our approach and the validation results were presented at several conferences. We also completed the development of our software application called Dynamic Real-time Ensemble Analysis and Monitoring (DREAM). This software allows modelers to launch and monitor an ensemble of numerical simulations. Additionally, while simulations are running, DREAM enables modelers to visualize and analyze the simulations in-flight. The integration of our statistical framework with DREAM effectively forms an uncertainty quantification pipeline. This tool is a core component in the GS^3 environment and will therefore be widely accessible for all GS^3 clients.

During FY 2013, we will add new functionality to DREAM to extend its visualization capabilities and its analysis capabilities. Additionally, we will submit several journal articles on both the analysis methods we have designed as well as the application we have built.

PN10079/2321

Nuclear Science and Engineering



A Virtual Testing Toolbox for Predicting the Properties and Behavior of Multiphase Materials in Disposal Environments

Joseph V. Ryan

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 it is a legacy of weapon development or the result of peaceful power generation. This project aims to produce a process whereby 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 naturally result in a large reduction in the cost 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) or when corroded by water (amorphous gel layer, crystalline corrosion products). Many 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 spatial arrangement of and relationship between various phases.

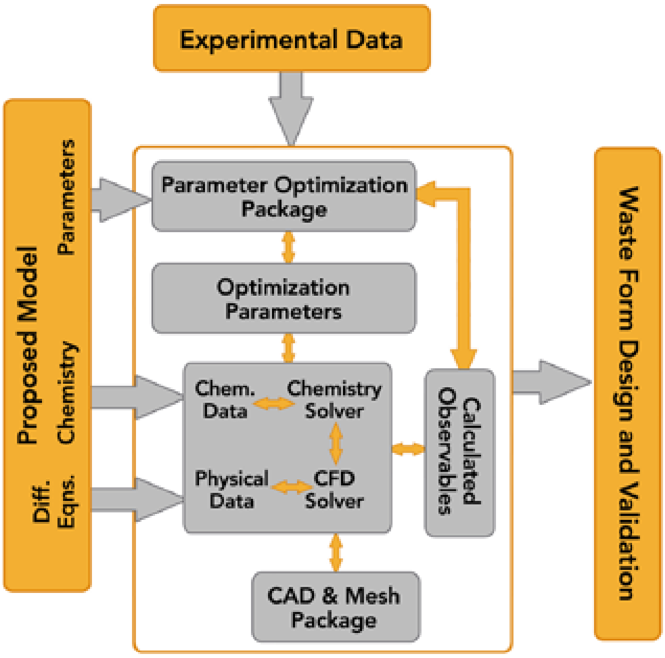
Materials and phases such as glass evolve into a system composed of bulk, surface alteration layers, near-field soil environment, and associated interfaces, where most (if not all) chemistries and compounds change from the original state. Similar processes occur for nearly every waste form.

Kinetics, where reaction rate constants describing the temporal evolution of a material into a new phase, creation of interfaces between phases, and 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.

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 assess product quality and long-term degradation mechanisms of multiphase waste forms and other multiphase materials in disposal environments. A generalized model evaluation tool is needed that allows proposed models to be systematically and quantitatively compared to experimental data and, just as importantly, to each other. The development of such a tool is described below.

The key to the tool is the development of methods for four powerful computational packages to exchange data rapidly and reliably (see figure). Modern engineering computational fluid dynamic (CFD) codes are used to handle mass and thermal transport in highly complex structures with



Schematic of the VTTB showing the relationship between different computational modules.

PN11005/2327

irregular natural or symmetrical man-made shapes at a variety of scales. These are robust, well-validated packages used extensively in chemical and mechanical engineering, where design validation is critical and legally necessary. Modern CFD codes generally do not handle complex chemical kinetics with great facility, however. Geochemical databases and programs such as Phreeqc and EQ3/6 provide extensive thermodynamic data for gasses, solutions, and minerals along with reasonable algorithms for solving reaction kinetics. Thus, handling reaction kinetics calculations with these programs while using CFD codes for transport calculations gives the advantage of utilizing the best aspects of each program while still looking at the system as a continuum structure. An interface to modern drafting programs (e.g., SolidWorks) allows the design and dynamic meshing of complex shapes.

We recently demonstrated the ability to integrate the necessary computational packages. Using artificial data, we integrated the COMSOL multiphysics CFD code with the newly available iPhreeqc library to evaluate a simple glass corrosion model. The PEST Gauss-Marquardt-Levenberg parameter optimization package was used to predict parameter values (with sensitivity analysis) from artificial experimental data by repeatedly running the COMSOL/Phreeqc model. The entire package was interfaced using MatLab that also handled data reporting and plotting.

The GRAAL model developed by the French atomic energy lab CEA is perhaps the most developed model to date that accounts for most of the experimental observations. A key objective of this project is to be able to evaluate models of other workers against appropriate glass dissolution experimental data. To this end, we set up and evaluated the GRAAL model using the VTTB, leading to a joint PNNL/CEA paper that is in final revision before submission to the *Journal of Nuclear Materials*. The GRAAL model consists of five differential equations that assume:

- the rate of glass erosion/dissolution is proportional to the silica supersaturation.
- the protective layer thickness grows slower as it gets thicker.
- a silica mineral phase forms at a rate proportional to supersaturation.
- silica as H_3SiO_4 in solution comes from dissolution but is removed by solution flow and mineral formation.
- boron in solution comes from dissolution but is removed by solution flow.

Note that the model does not explicitly include any chemical reactions and as such the iPhreeqc module does not have to be used in this instance. This is an acknowledged major drawback to this version of the model, and new models are being developed by CEA that directly take into account chemical processes.

The fit to the data was poor at best depending upon the particular data set examined. This indicates either an inappropriate model, one that is missing essential physical representation, or difficulty in obtaining reproducible data. From this project's perspective, the results allow close examination of the experimental data and comparison with the model. Ferreting out why a model does or does not reproduce a set of experiments requires much more detailed investigation, including development of new models, than was possible in this project. We note that new depth profiling techniques that can map the spatial distribution of glass species within the altered layers provide invaluable information and the VTTB can incorporate this data as well as the more common concentration of dissolved species.

The results were presented mid-year at two international workshops for glass corrosion. The successful demonstration of the potential of VTTB led to the awarding of competitive programmatic funding to develop it further for high-level waste glass corrosion issues and to analyze existing models with the inverse modeling techniques.

In addition to the modeling task, experimental work from a couple of years past on cementitious multiphase waste forms was written up and submitted to *Waste Management*. These materials (e.g., cast stone, salt stone) 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 as a function of simulated secondary waste solution loading. This work showed that the cast stone material can immobilize a wide range of waste loadings with no appreciable change in effectiveness.

Advanced Condition Monitoring of Microstructure Evolution and Property Degradation in Current and Advanced Nuclear Reactor Alloys

Shenyang Hu

We are developing mesoscale phase-field models for studying the effect of microstructures on material response to applied fields, understanding signal physics in nondestructive examination (NDE), and providing guidance for developing real-time nondestructive detecting/monitoring methods.

Important scientific and technological breakthroughs are needed in characterizing, detecting, and understanding the early phase of environmental degradation in materials used in nuclear reactors. Environmental material degradation is one of the main concerns impacting the performance, reliability, and safety of structural materials in these units. In FeCr alloys and zirconium, the preferred candidates for structural materials in fusion and advanced fission reactor components, irradiation-enhanced phase separation (the formation of Cr rich precipitate, Carbides, and hydride precipitates) causes materials embrittlement, the reduction of corrosion resistance, and creep failure. Therefore, predicting the kinetics of microstructure evolution, understanding the degradation mechanisms, and developing a real-time monitoring capability of property degradation are key milestones to managing existing nuclear power plants.

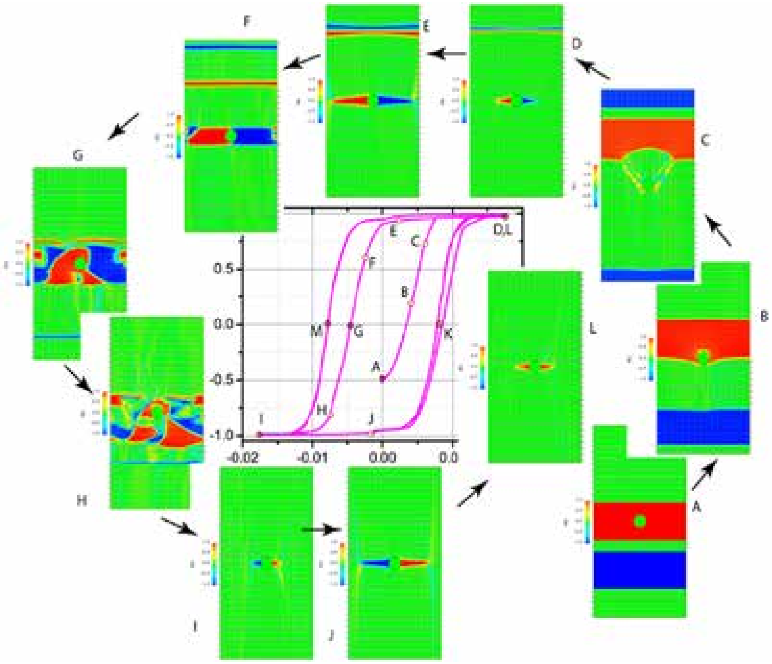
The objective of this project is to develop advanced modeling tools for investigating the impact of initial microstructure and environment conditions on microstructure evolution kinetics; the effect of microstructure on material response to applied fields such as ultrasonic and magnetic fields; signal physics in nondestructive examination; and critical degradation mechanisms and key precursor states.

During FY 2012, we developed a phase-field model to study the magnetic domain wall stability and interaction between magnetic domain walls and nonmagnetic particles. FeCr alloy is taken as the model system. The nonmagnetic particles/precipitates could be Cr rich precipitates, carbides and voids which are formed during irradiation-induced phase separation in FeCr alloys. The magnetization vector **M**(**r**,*t*) is used to describe the spatial and time distribution of magnetic domains. The magnetic domain evolution is simulated by solving the Landau–Lifshitz–Gilbert (LLG) equation. The figure summarizes the predictive magnetic hysteresis loops and magnetic domain evolution in a BCC single crystal iron with a nonmagnetic particle.

In these models, a simulation cell of 256 nm × 512 nm × 1nm with periodic boundary conditions is used. The simulation shows the following: 1) 360 degree domain walls are stable in a single crystal under applied magnetic field in easy magnetic axis; 2) both 360 degree domain walls and nonmagnetic particles are nucleation sites of a new anti-direction domain during domain switching; 3) a new anti-direction domain nucleates by splitting a 360 degree domain wall much easier than from a nonmagnetic particle; 4) nonmagnetic particles can destroy the 360 degree domain wall, which causes magnetic hardening; and 5) nonmagnetic particle can pin and bend a domain wall when the wall passes through it and thus inhibit domain switching.

The main achievement in FY 2012 is that we developed and demonstrated new modeling capability to investigate the interaction mechanisms between nonmagnetic particles and magnetic domain walls and explore the signal physics in nondestructive magnetic techniques used for monitoring microstructure evolution in irradiated materials.

Our overall goal is to establish PNNL as the leader in material degradation detection of nuclear materials.



Initial magnetic domain structure in (A), including 90 degree domain walls and a nonmagnetic particle, is created. The color represents the magnitude of the M_z component, and arrows represent in-plane projects of the magnetization vectors.

PN12004/2405

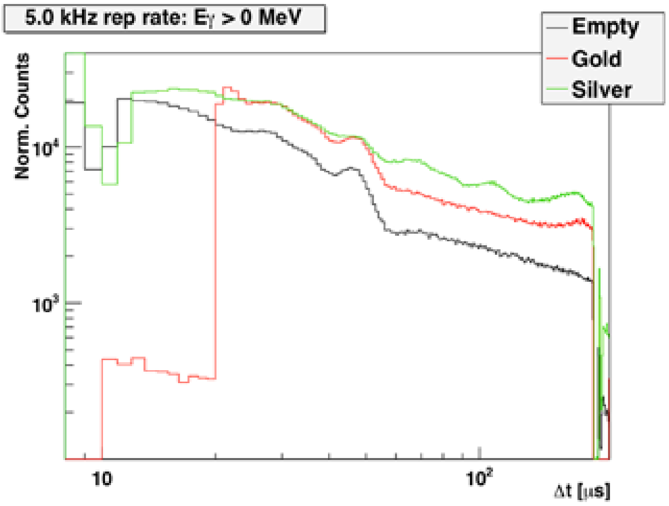
Advanced Nondestructive Assay for Safeguards

Glen A. Warren

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 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 (10s 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 expands 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. 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 as 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

PN10004/2246

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.

Though the project was cancelled in early FY 2012, the most significant accomplishment was the acquisition of a deuterium-tritium neutron generator with the appropriate time structure to conduct LSDS measurements. Project leadership has been exploring options to fund completion of spectrometer characterization as well as assessing the use of project capability in support of other client-funded efforts.

PN10004/2246

Argon-39 Measurement

Paul H. Humble

This project is developing and implementing an ultra-sensitive argon nuclear measurement capability that has relevance to environmental age dating, fundamental science, and national security applications.

Argon is commonly used as a fill gas in gas-proportional counters and liquid argon scintillation detectors. ^{39}Ar is the longest-lived radioactive isotope of argon with a half-life of 269 years. Due to its lengthy life and generation by cosmic ray activity, ^{39}Ar can be a major source of background activity in ultra-sensitive nuclear measurements when used as a fill gas in proportional counters or in scintillation detectors. With this method, it is desirable to have a source of ancient argon depleted in ^{39}Ar and have a detection capability with enough sensitivity to measure ^{39}Ar activity. An ultra-sensitive ^{39}Ar measurement would also provide the opportunity for age dating water or trapped atmospheric gas in the timeframe between 50 and 1000 years.

The major objectives of this project are to develop an ultra-sensitive ^{39}Ar nuclear measurement capability and formulate a reliable source of ancient (^{39}Ar depleted) argon for use in gas-proportional counters. Possible sources of ancient argon include dissolved gas in deep ancient aquifers and argon trapped in natural gas reservoirs. The most promising source of low activity argon at this time appears to be select natural gas wells. This resource is being developed by Fermi National Accelerator Laboratory (Fermilab) to construct dark mater detectors, and we are collaborating with Fermilab to measure ancient argon that they have processed and purified for this purpose. During the next several months, we will develop a high recovery argon separation and purification process that enables extracting argon from small gas samples including dissolved gasses in water. This capability will benefit argon measurements for environmental as well as national security applications.

The ultra-sensitive ^{39}Ar measurement capability leverages the shallow underground laboratory and work being done on other ultra-sensitive initiative projects to develop low background materials and proportional counters. For this project specifically, operating parameters and analysis packages are being developed to provide ultra-sensitive measurements of ^{39}Ar activity. This capability is being extended to enable ultra-sensitive measurements of other Ar isotopes, including ^{37}Ar, which has importance in nuclear explosion monitoring.

The expected results from this project are a demonstrated Ar nuclear measurement capability and the identification of an argon source with low ^{39}Ar activity that can be used in ultra-sensitive gas proportional counter work. Thr project began mid-year, and the scope for this short time was to set up the necessary proportional counters, develop operating parameters, devise an analysis package, and finally measure the ^{39}Ar activity of a gas sample provided by collaborators at Fermilab. We are in possession of the Fermilab gas sample, and these objectives will be accomplished before the end of the year.

Also during FY 2012, we set up the capability to make ultra-sensitive Ar measurements in gas proportional counters. And have successfully made measurements on argon extracted from laboratory room air. We have also received a gas sample from Fermilab that contains argon they have separated and purified form a natural gas well. This gas should contain low activity ancient argon, and this will be confirmed.

In the first quarter of FY 2013, we will publish the results obtained from the Fermilab gas sample. We will work toward making other argon activity measurements, and develop argon calibration sources. We will also start work on a high recovery argon separation and purification technique that would be of significant benefit for separating argon from small purposes such as dissolved gasses or environmental samples. We expect to have one or more publications describing the sensitivity of our argon measurements as well as a method to separate and purify argon with a recovery greater than 80%.

Background Reduction for Nonmetallic Nuclear Detection Components

Raymond Addleman

The world's most sensitive radiation detection and assay systems depend on ultra-low background (ULB) methods and materials to achieve their remarkable sensitivities. ULB systems have application to basic science efforts such as neutrino, dark matter studies, and practical functions in nuclear forensics and environmental science.

Ultra-low level radiation detection systems need better supporting materials (structural, mounting, electrical) that provide lower radiological backgrounds. We explored new methods to provide ultraclean nonmetallic components that will enable ultralow-level measurement systems. Radio-impurities currently used to construct ULB systems both on the surface and in bulk material continue to limit the lowest backgrounds achievable. Significant effort has gone into finding and processing ULB metals such as Pb, Cd, Cu, and steel that act as shielding and supporting materials as well as critical detector components. Much less effort has gone into finding or generating nonmetallic ULB materials that provide essential electrical and thermal insulation for nuclear detection systems and can provide physical support structures. Nonmetallic materials could be advantageously used if ULB levels could be achieved. In this important and promising area, improvements in radiopurity of three orders of magnitude (from mBq/kg to µBq/kg) are needed and if achieved would be widely utilized in the ULB systems. The main contaminates of concern are isotopes K, U, Rn, and Th and their respective progeny. Ideally, nonmetallic materials of interest could be found or provided at 10 µBq/kg.

The focus of this effort and key technical challenges for finding and providing nonmetallic ULB materials of sufficient radiopurity are as follows:

- Accurate assay of contamination levels. The point of this effort is to identify and provide ULB materials to the scientific community, which in turn requires accurately measuring inorganic contaminates in diverse organic matrices at ULB levels, a nontrivial challenge that must be addressed. Effective assays will enable materials of interest to be screened effectively for contamination and support development of purification methods (should clean sources of desired materials not be found). Various analytical methods and approaches need to be evaluated comparatively.
- Identifying source(s) of contamination and means to avoid them. Some materials may be identified with background levels intrinsically low enough that they can be used directly. In most cases, however, sufficient radiopurity levels will not be available, and the location (surface, bulk) and likely origins (monomer feedstock, polymer synthesis, material processing, handling) will have to be determined before methods to clean the material of interest can be formulated. Once the location and source of contamination is known, methods to avoid or remove contamination and achieve ULB levels can be developed rationally.
- Development of methods to remove contamination. It is likely that contamination will be unavoidable. In these cases, purification methods will have to be developed for materials of interest.

In FY 2012, we made progress on all key technical challenges identified above. The majority of activities focused on development of accurate ULB assay methods, which is a necessary capability to support all other efforts. We found traditional nuclear counting methods such as gamma ray spectroscopy required prohibitively long count times for the ULB assay, even when underground detector arrays are available. Digestion of nonmetallic sample removes the matric, concentrates contaminates, and enables traditional ultra-trace chemical methods such as inductively coupled plasma mass spectrometry (ICPMS) that is capable of rapid analysis and high sample volume throughput. Sample preparation and handling methods are critical for obtaining meaningful results. Productive ULB chemical process methods have been developed and are successfully demonstrated on a number of polymeric materials of interest, with ICPMS detection limits below 10 ppq (for U and Th). Additionally, the chemical preparation processes have applications to other analytical methods such as alpha spectroscopy, an excellent technique for radon (and daughter products) contamination detection.

Contamination sources and the means to remove and avoid the impurities were also explored. Adapting PNNL-developed methods for ULB copper, we explored leaching U and Th, primary contaminates of concern, from polymers. Using ultrapure nitric and hydrochloric acid, we found that we could remove surface contamination (i.e., from mineral dust) after 2–3 days of rinsing without damaging the polymer. This cleaning method has application for the reduction of background in polymers ranging for powdered feedstock to final cleanup of machined parts.

To disseminate the results and information gathered to the greater scientific community, several publications – one focused on analytical methods and another on polymer cleaning techniques – will result from FY 2012 activities.

PN12011/2412

BazookaSPECT Neutron Imager

Brian W. Miller

We seek to develop high-resolution ionizing radiation detector technologies for use in medical imaging, nuclear science, and national security applications.

During the last several years, a new class of gamma-ray detector, BazookaSPECT, has been developed that combines columnar scintillators, image intensifiers, and charge coupled device/complementary metal oxide semiconductor (CCD/CMOS) sensors for high-resolution imaging. This detector has primarily been employed in pre-clinical medical imaging applications, and we are now interested in exploring and characterizing its use for detecting additional forms of ionizing radiation (e.g., neutrons, alpha particles, fission fragments, betas, and conversion electrons) for use in national security and nuclear science applications.

As BazookaSPECT is becoming a next-generation detector for gamma-ray imaging applications, a natural extension of the technology is to research its capability as a neutron imaging detector, particularly in applications that will benefit from its high-resolution capability. Gas electron multipliers (GEMs) are another promising detector technology that we are investigating. GEMs provide excellent timing, spatial resolution, and high count-rate capabilities and can be fabricated in large areas at low cost. We are particularly interested in investigating GEMs as a potential Helium-3 replacement technology for thermal neutron detection applications. Our objective of this project is to establish these two detector capabilities at PNNL and investigate, demonstrate, characterize, and improve their detection response to ionizing radiation. We will also seek to develop applications that are enabled/or improved upon by the technologies.

During FY 2012, we initiated the process of bringing BazookaSPECT and GEM detectors to PNNL. A CERN GEM detector kit has been ordered and should arrive at the end of FY 2012 or early in FY 2013. The detector read-out electronics are provided separately, and we are currently on a waiting list and anticipate arrival early FY 2013.

We have acquired BazookaSPECT components and are currently assembling the detector, which we anticipate to be fully functional in early FY 2013. We have modified the detector acquisition software to support the newly released USB 3.0 CMOS cameras, which increase the event detection rate by 2 times. The BazookaSPECT detector was originally developed for use in pre-clinical medical imaging applications, and we are establishing collaborations within PNNL with groups who are interested in the small-animal imaging capability.

Recently, a major breakthrough occurred in the design of BazookaSPECT that has led to the development of large-area detectors (> 10 cm in diameter), which can be used to perform full-body, dynamic scintigraphy of rodents. Late in FY 2012, we were invited to present the concept/design of the prototype detector at the SPIE Optics + Photonics conference. The detector currently being assembled will also have this capability.

We initially proposed investigating both the BazookaSPECT and GEM detectors for use in neutron detection and imaging applications. Instead, we are currently expanding their role, particularly BazookaSPECT, to include additional forms of ionizing radiation previously mentioned: fission fragments, alpha particles, betas, and conversion electrons. In FY 2013, we will demonstrate the capability of BazookaSPECT to detect these additional forms of ionizing radiation, and we will measure the detector's performance in terms of energy and spatial resolution. Various scintillation materials will likely be tested during this process. Some potential applications that we will investigate include coincidence detection of different particles/photons that can be used to identify and separate isotopes, spectrometry, and small-animal planar scintigraphy.

Once the GEM detector and read-out electronics arrive, we will familiarize ourselves with the detector and GEM acquisition software provided by the CERN RD51 collaboration. This will include some initial low-energy x-ray imaging experiments to determine the spatial and energy resolution of the detector. As we become familiar with GEM technology, we will being design of a new GEM detector or modification of the CERN kit that can be used for detecting thermal neutrons.

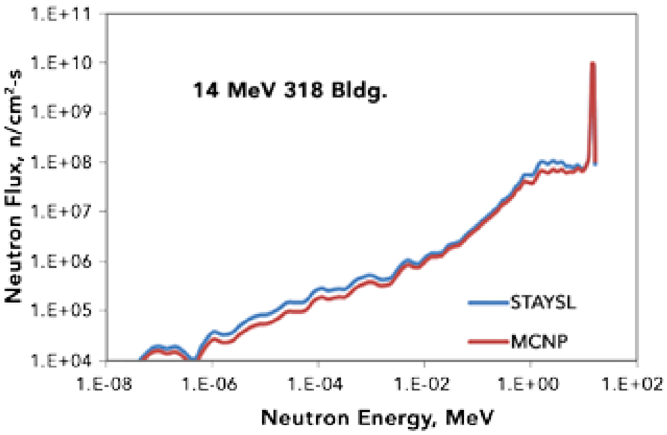
PN12012/2413

Characterization of a 14 MeV Neutron Generator and Measurement of Fission Products Produced

Erin C. Finn

The recent installation and characterization of a 14 MeV neutron generator at PNNL has enabled nonproliferation research and development (R&D) by supporting the production of unique radionuclides for use with several nuclear advancements, particularly the measurement and evaluation of possible new short-lived isotope signatures.

Historically, PNNL's efforts in nuclear nonproliferation R&D have been thwarted by a lack of readily available, correct radioactive standards and realistic radioactive samples that are needed to accurately test new measurement and data evaluation methods and improve nuclear data. The 14-MeV neutron generator was purchased and installed in the 318 Building low-scatter facility using general research equipment funds. The facility housing the generator is unique and enables us to achieve a very pure 14 MeV neutron spectrum with minimal scatter. Before the new generator can be used to produce samples required for high accuracy nuclear measurements, the instrument must be set up and characterized to ensure a consistent high flux of pure 14 MeV neutrons.



Modeled (MCNP) and experimental (STAYSL) neutron spectra at the D-T 14 MeV neutron generator face housed in the 318 Building low-scatter facility. Results show good agreement at 14 MeV; however, experimental measurements indicate an increase of 10–50% in the number of scattered neutrons over the MCNP model. Scattering is expected to become more pronounced at greater distances from the generator face.

The objective of this work is to make the generator capability available to a diverse user group. Securing capability requires that all appropriate procedures and permits are in place, along with an understanding of system operation and what results to expect from various operating schemes. To accomplish this, Monte Carlo N-Particle (MCNP) modeling is used to predict the results, which are then experimentally tested and validated.

Effective experiment planning requires a baseline series of quantitative experimental measurements of the neutron environment, flux, and spectrum available. Such measurements are made using standard dosimetry techniques, wherein high purity wires or foils with known neutron activation cross-sections are irradiated under known conditions. The activation of the materials is measured by gamma spectrometry and used to calculate the number of neutrons incident on the sample. Use of multiple materials concurrently allows measurement of the neutron spectrum in addition to the neutron fluence.

All applicable permits and procedures are in place, and the neutron generator was approved for use early in FY 2012. MCNP modeling has been completed to provide preliminary estimates of neutron flux and spectra at various positions relative to the generator. These models show that the neutron flux and neutron spectra change measurably with change in position relative to the central point of the generator head. In addition, experimental measurements are underway to validate the effects predicted by the MCNP models. We completed a short series of measurements at the central point for different operating parameters and will measure at different positions at known sets of operating conditions. At the central point on the neutron generator face, total neutron flux measures 1.53 × 109 n/cm^2/s (±5%) at the maximum operating power. The neutron flux is broken down into the following energy bins:

4.43 × 104 n/cm^2/s (±24%) thermal (< 0.5 eV)

9.00 × 106 n/cm^2/s (±15%) epithermal (0.5 eV to 0.1 MeV)

2.51 × 108 n/cm^2/s (±10%) fast (0.1 to 10 MeV)

1.27 × 109 n/cm^2/s (±5%) fast (>10 MeV)

Mid-year 2012, the neutron generator successfully produced short-lived radioisotopes for one of the projects.

Operation of the neutron generator caused dose in adjacent spaces in the facility, negatively impacting existing projects in those spaces. We received some funding for the generator space shielding, and additional funding was acquired through other sources to further mitigate this problem and prevent future negative impacts on other projects. However, initial characterization of the neutron generator enabled one of the projects to achieve its highest impact milestone. The generator produced isotopes that have not been available to this project in the past, facilitating more complete testing and demonstrations of the project's scientific advancements than had been possible previously. Other projects are also planning experiments using the initial characterization data.

The remaining characterization work is expected to be completed using dosimetry techniques in FY 2013, followed by publication of the data on this unique capability. Plans for later in FY 2013 include the design and performance of gamma spectrometry experiments on fission product samples, which will enable us to determine the fraction of fissions produced from 14 MeV neutrons, fast, epithermal, and thermal neutrons. This research is expected to yield a second publication.

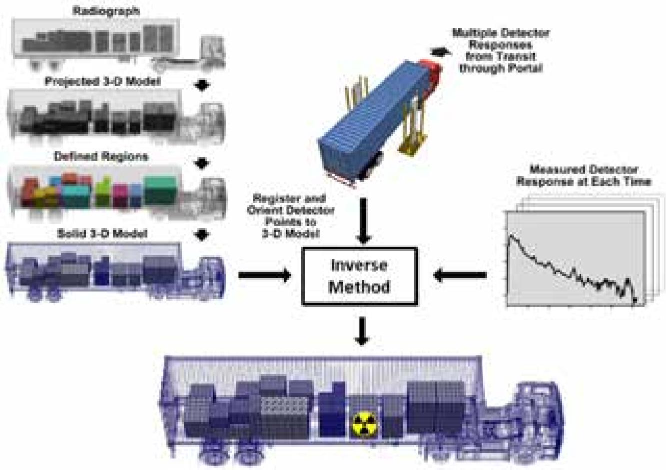
Exploiting Correlated Radiographic and Passive Signatures for Threat Detection in Cargo

Erin C. Miller

This project develops methods to improve radiological threat detection in cargo containers by systematically combining information from passive radiological sensors and radiography. Both techniques are currently deployed for cargo screening and are widely acknowledged to provide complimentary information.

We are developing an inverse algorithm for describing a possible radioactive source in cargo using radiographic and passive portal monitoring data. Our method developed may provide a quantitative and cost-effective way to harness this information. Currently, cargo radiography is used to detect contraband but not radiological threats. Previous work on combining radiography and passive sensors for cargo has largely focused on high-level data fusion, where both pieces of information are evaluated separately. This work builds off a previous project that developed a source localization algorithm for combining multiple passive sensors, given some estimate of attenuating or scattering materials. We are investigating the use of radiography for providing information about the problem geometry, with an emphasis on cargo screening.

Research on this project covers three key areas: first, developing a method for making a 3D geometry estimate from a radiograph and evaluating the impact of this approximation; second, investigating the possibility of low-dose radiography with poor spatial resolution to provide this kind of shielding geometry estimate; and finally, developing detection metrics for quantitative comparison with existing algorithms. These pieces will allow us to evaluate the feasibility of our approach and its sensitivity to the quality of the geometry estimate, lay the groundwork for future injection studies of the method, and provide the basis for scientific publications.



Method: Portal monitor responses and radiography are combined in an inverse algorithm to describe source location and position.

Work in FY 2012 focused on a model test case (a cargo container with pallets, some of which contain a material that attenuates and scatters radiation). Detector response for a portal as the cargo is driven through was calculated; radiographs for the cargo container under high- and low-dose conditions were calculated for pixel sizes ranging from 3 cm (similar to a currently deployed MobileVACIS) to 20 cm. Adjoint calculations describing the contribution of a source at any point in the container to a particular detector were determined for multiple scenarios: perfect information about geometry, geometry information obtained from a low-dose radiograph, and treating the cargo as a homogenous mass. Perfect geometry information with attenuation only accounted for (scattering ignored) and with ray-trace only (scattering and attenuation ignored). Preliminary results indicate that the ability to locate a source is improved when knowledge of geometry is improved, but only when signal-to-noise is sufficiently high. Several preliminary detection metrics have been developed that will be used to produce receiver-operator curves for comparison with current detection algorithms. This progress will also enable us to judge whether the new algorithm provides improvements and what kind of geometric detail and accuracy of transport physics is needed.

Work in FY 2013 will focus on a more complex test case, with an attenuating object as a source to include background radiation from cargo in addition to a potential threat. Additionally, quantitative comparisons with current methods will be produced. These results should allow us to evaluate the feasibility of our algorithm and the low-dose radiography when used for the detection of radiological threats.

PN12030/2431

Isotopic Ratio Fluence Monitors for Canadian Deuterium Uranium (CANDU) and Pebble Bed Modular Reactor (PBMR) Plutonium Production Verification

Mark R. Mitchell

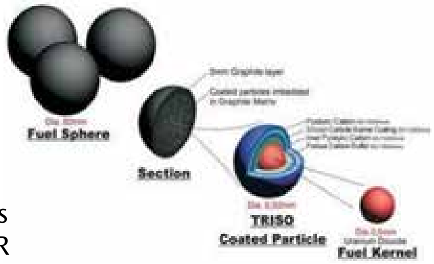
We are developing a concept to create monitoring devices that can be attached to reactor vessels, in-core structures, and techniques to analyze existing reactor materials, enabling quantification of plutonium with accuracy for safeguard purposes without direct fuel analyses. These technologies will provide a method for objective verification of adherence to declared reactor operation.

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. Thus, we are developing techniques for both reactors and fuel assemblies that should make 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 Advanced Test Reactor (ATR), followed by PNNL analysis 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 assemblies with a length of 0.5 meter.

The design of CANDU reactors presents unique nonproliferation and safeguards challenges. The small physical size of CANDU fuel bundles, their short duty cycle, and the ability of CANDU reactor to be reloaded in operation complicate item accounting compared to light water reactors (LWRs). PBMR reactors are less of a proliferation threat but pose additional safeguards due to reactor design. PBMR uses fuel pebbles rather than traditional pellets housed in fuel rods like LWRs. The sheer number of fuel elements presents an accountability challenge.



Construction of PBMR fuel.

The main accomplishment in FY 2009 was shipping graphite samples to MURR. For FY 2010, primary efforts included packaging graphite samples for irradiation at MURR and presentations of the work. The first MURR sample was shipped to PNNL in late 2010, and the aluminum capsule was opened in a glove box. The capsule was high in activity, which delayed unpackaging. Graphite samples from this first exposure package were 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 was prohibitive. The team investigated metals irradiation at the ATR. Meetings with Chalk River Laboratory 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 pressure tubes. These circumstances combined to make analysis of Zircaoly impurities, as we have previously investigated for LWRs, more practical than investigating a purpose-built indicator that AECL would be reluctant to use.

In FY 2011, the remaining samples irradiated at MURR were removed at two intervals for analyses. Preliminary measurements were made in late 2011 and continued into 2012. Initial measurements indicated an ion present with a mass of 10 AMU consistent with beryllium 10. We expect to find some beryllium transmuted from carbon by high energy neutrons, and we anticipate being able to measure titanium isotope ratios. When measurements are complete, we can draw conclusions about the relative value of beryllium in the irradiated carbon as a fluence indicator. Availability of the Cameca 4f SIMS has not been sufficient to finish analysis mostly due to needed repairs. We will complete the analysis and publish at least one journal article before the end of 2012.

CANDU work is moving forward as a DOE-funded project, and discussions have occurred with Chalk River for collaboration regarding isotope ratio studies of the scraping samples. Additionally, the team measured titanium as well as zirconium isotope ratios, the latter of which may be a good method to measure the relatively high fluence to which the pressure tube has been exposed after several years of operation.

PN09042/2210

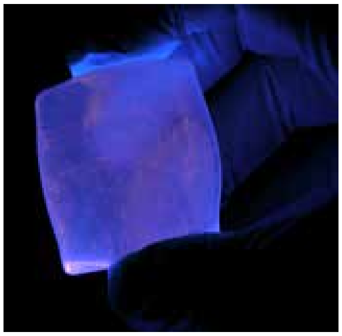
Novel N/Gamma Flux Monitoring Materials for Safeguards and Proliferation Detection

Mary Bliss

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 ratio is useful in monitoring and identifying various types of special nuclear material for Arms Control Treaty verification and 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 3He detectors, advanced formulations of enriched glass that simultaneously detect thermal neutrons and gamma rays. Energy windowing will be applied to gain information from gamma ray signals. New signal processing electronics and algorithms will also 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 it was unknown if bulk pieces could be routinely produced without clouding from phase separation. 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 for this project, along with pairs of blue and red enhanced Hamamatsu single photon-counting 2.5 cm diameter photomultiplier tubes. Prior to PIXIE, an older system was used to characterize the samples, which were mounted to blue-enhanced PMT using optical coupling grease. The PMT and sample are 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 inches of lead shielding was used to suppress gamma rays. Cadmium foil suppressed thermal neutrons. A ^{137}Cs source was used for gamma ray energy calibration and response.

Pulse-shape processing. Each light-generating event is recorded with the time windows on the order of 5 ns, 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 issue is defining pulse shape to maximize differences between gamma rays and neutrons. Along with pulse shape analysis, Raman spectroscopy was used to explain variations in scintillation light output with glass composition. Analysis indicated that the glass samples contain up to three distinct glassy regions with only one correlating to scintillation brightness. Stacking two disks of glass did not significantly change the appearance of the pulse-shape processing data.

Further research is needed to understand more succinctly the nature of the pulses that appear between the neutron response cloud and the gamma ray response. This may be due to recombination of excited states (non-proportionality), thermal depopulation of long-lived excited states, or the neutron capture by products escaping the material. These results show that bulk enriched lithium glass can be used as a higher performing thermal neutron detection material than previously thought. Our work was published in the *Journal of Non-Crystalline Solids* and presented at an international conference.

PN11059/2381

Three Dimensional Neutronics Analysis Capabilities for Nuclear Archeology Applications

Christopher J. Gesh

> ***Nuclear archeology is a vital capability that the United States needs for many missions, including arms control, nonproliferation/verification, and the commercial nuclear power industry. While PNNL is the leader in developing nuclear archeology methods, significant work is required in maintaining a current, fully operational and robust national laboratory capability.***

Nuclear archeology is the measurement based study of nuclear facilities to determine historical information and past operating history to confirm a facility operator's declaration independently. One of the key nuclear archeology techniques used at PNNL is the isotope ratio method (IRM), which estimates the energy or plutonium production in a fission reactor by measuring stable isotope ratios in non-fuel reactor components and relating those ratios to neutron fluence at the sample locations. Based on the fluence and sample location, reactor numerical models are used to calculate the integrated energy or plutonium production of the reactor. Increasing the fidelity of the neutronics analysis allows for more accurate assessments of the reactor operation and use of samples from a wider variety of locations.

This work establishes baseline computational models, methods and capabilities for the current three-dimensional transport codes required to provide timely response to program requests and to establish reasonable expectations from the process. Though the computational approaches are well established, applying them to complex, full-core, high-fidelity depletion problems is challenging and continues to advance with better computing hardware. Maintaining a core staff with a competitive skill set in the rapidly advancing nuclear analysis field requires regular exercise and training of new staff.

Multiple analytical approaches are being studied to identify the strengths and limitation of each. The computer codes considered to date are 3DB (diffusion theory and the current state-of-the-art), MCNPX/MCNP6 (Monte Carlo transport) and Attila (discrete ordinates transport). First, a 3DB model for a generic MAGNOX reactor has been completed and will be used to compare with subsequent discrete ordinates and Monte Carlo results.

MCNPX and MCNP6 models of a MAGNOX reactor and the Hanford B-reactor were used to document sensitivities of the results to the number of burn zones, temperatures, number of fission products tracked, running time, convergence of the power distribution, and the like. These parameters will be useful in quantifying uncertainties in this type of calculation. Measured fuel isotopics as a function of burnup for B-Reactor was located and will be used to validate the MCNPX/CINDER and MCNP6-beta modeling. This information will be compared with subsequent discrete ordinates results.

A MAGNOX core model was successfully imported into Attila, where the mesh has been generated and materials assigned. Developing a suitable burnup cross section library has been found to be more problematic than originally expected. A parametric study was conducted on the Attila Magnox model in order to determine the sensitivity of input parameters to the resulting calculated k-eigenvalue. In addition, Triton (part of the SCALE code package) is being used to develop case specific cross sections for Attila depletion. The development of suitable cross sections remains a priority for the IRM work and for the FY 2013 scope that involved ex-core, in-vessel thermal fluence modeling.

Work continues in the documentation and result comparison between the codes and methods. Two papers (one involving the use of measured IRM data to support nuclear cross section improvement and one summary of IRM neutronics methods) are planned for FY 2013. The work will be coordinated with another project to apply the tools developed to specific problems of interest. The client has expressed interest in using this results of this project to model an IRT reactor that will be subjected to IRM sampling during summer 2013.

PN12076/2477

Ultra-Low-Background Gas Measurement: Building an Advanced Capability

Allen Seifert

We are developing an ultra-low-background (ULB) measurement capability for gases available to basic science and emerging application areas, leveraging our new facilities and achieving scientific competitiveness on an international level. This work builds capability for diverse new applications, resolves unique measurement challenges, and will result in high-impact demonstration measurements.

Extremely sensitive nuclear measurements are exploited in a number of scientific disciplines. Measurements of low levels of radionuclides in the environment allow their use as tracers and for age dating. Examples include studies of fate and transport of dust (^{7}Be) in the atmosphere, deep-ocean mixing (^{39}Ar), estuary and deep ocean sedimentation (^{32}Si), soil erosion (^{7}Be), and studies of the mechanisms and pathways for carbon fixation by soil biota and residence times for organic and inorganic carbon (^{3}H, ^{14}C). Low-level measurements are also useful in the verification of nuclear treaties; e.g., detecting ^{37}Ar produced by an underground nuclear test. Across all of these areas, the need for greater sensitivity is paramount.

ULB proportional counters have been used for decades for samples that can be prepared as gases and are particularly sensitive to low-energy beta and electron emitting radionuclides. Recently, PNNL developed a design with improved radiopurity materials, and this project moves forward from that foundation. High-sensitivity measurement methods will be developed for specific isotopes, and the detector design will be enhanced to allow greater sensitivity. As an example, a measurement of combined tritium and ^{14}C in methane will be developed, which will allow these radiotracers to be used in the study of hydrocarbon compounds in soil bacteria. Analogously, this project will develop the gas handling and quantification tools necessary to work with a variety of input gases derived from other environmental samples. The suite of ULB proportional counters necessary for these high-sensitivity demonstration measurements will also be constructed, with design improvements incorporated as they are developed. The ultimate goal is the development of an enduring ULB capability for the measurement of environmental samples at PNNL that will position the Laboratory to compete with other recognized leaders around the world.

For this project, FY 2012 began with the development of hardware to enable high-sensitivity demonstration measurements. Specifically, construction began on a general-purpose gas-handling system designed to handle a broad range of sample types, with evolution of the gas processing capabilities planned for each year of the project as new demonstration measurements are identified. The first such development for the gas-handling system happened late in FY 2012, as a large-volume transfer system was added to enable ^{37}Ar and ^{39}Ar. A successful demonstration, also at the end of the FY, proved the ability to load custom blends of an argon-based count gas into the ULB detectors.

Five ULB detectors were constructed this year to enable innovative new measurements. Significant effort was put into characterizing and optimizing performance of the new detectors at pressures and gas gains higher than previously employed. These new operating parameters allow for the introduction of greater quantities of sample and thus provide an increased sensitivity to low-level samples. The combination of these new settings and new gas-loading capabilities enabled sensitive measurements of samples of opportunity of ^{37}Ar and ^{39}Ar.

An observed gap between modeled and experimental detection efficiency offers the opportunity for significant gains through modeling and design work. Thus, a modeling effort was undertaken to understand factors in the current design contributing to fiducial volume losses. The detector electric field has been modeled with Ansoft's Maxwell3D finite-element software, with further work planned using the Garfield gas detector simulation code to investigate pulse formation and detector end effects.

Activities planned for FY 2013 will develop calibrated, ultra-sensitive methods for specific measurements. Optimization of the operating parameters and performance of the ULB proportional counters will allow key radiotracer measurements (^{37}Ar, ^{39}Ar, ^{3}H/^{14}C) in parallel projects at previously unattained sensitivities. Further development of the gas-handling system will be aimed at precision quantification of gas samples. The ULB proportional counter design will be refined to allow operation at higher pressures, and detector electronics capable of operation at the correspondingly higher voltages will be developed. Finally, novel uses of the ULB proportional counter will be explored, such as utilizing ^{3}He to enable low-background neutron detection.

PN12078/2479

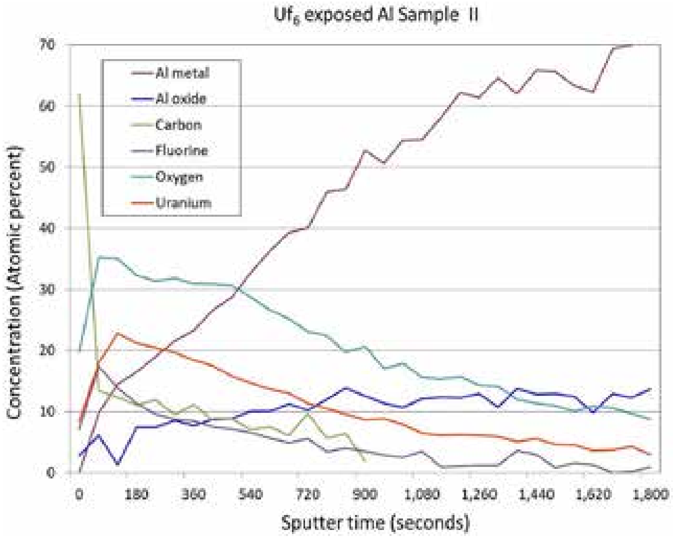
Uranium Enrichment Facility Signature Exploitation

Bruce D. Reid

A number of countries with uranium enrichment technology are not signatories to the Nuclear Non-Proliferation Treaty or have dubious nonproliferation credentials. A technology for validating enrichment production history could have a valuable application for resolving the international concerns associated with these facilities.

There does not currently exist a robust measurement technique for determining the throughput and operational history of an uranium centrifuge enrichment facility. The nonproliferation community has recognized that an ability to assess past enrichment facility operations is a “holy grail” of the nonproliferation verification challenge. It has also been previously noted that it may be possible to gain some understanding of the throughput and enrichment of enrichment plants through examining facility piping. With these challenges, this project is maximizing a signature inside a centrifuge to provide a unique method for estimating past enrichment plant operations. This applied science investigation is using PNNL’s surface science expertise to quantify material production at a uranium enrichment facility. Additionally, this study will furnish a scientific basis for assessing the ability of various archeological techniques for accurately predicting the throughput and enrichment of the enrichment facility.

Significant time during FY 2012 was dedicated to developing the necessary collaborations with Oak Ridge National Laboratory and the University of Virginia to accomplish future objectives. Coordination with the United Kingdom Department of Energy and Climate Change was also established to obtain actual enrichment facility hardware for the purpose of project analysis. The results of these collaborations are encouraging, with the project expecting to receive piping and a pump for FY 2013. DOE/NNSA client engagement has been positive, and additional limited funding is expected to maintain the relationships with the above mentioned institutions.



X-ray photoelectron spectroscopy concentration as a function of sputter time.

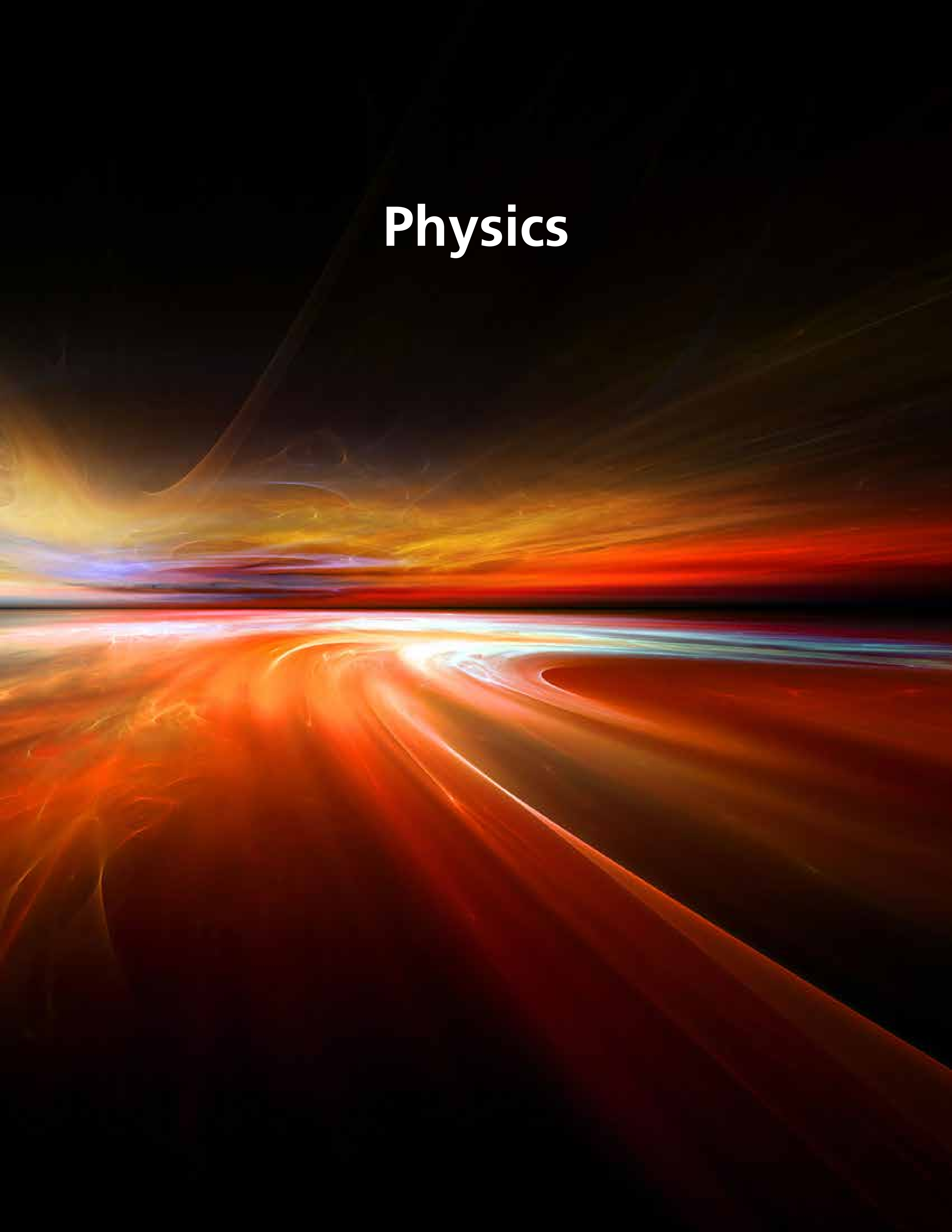
The project’s initial measurements have been completed with promising results. The current methodology for the combination of scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and time-of-flight–secondary ion mass spectrometry (TOF–SIMS) provided corrosion/passivation isotopic ratios, elemental ratios, and quantity of uranium. Additional testing is underway to determine the level of accuracy expected with this combination.

The literature searches are complete. This provided detailed background in about uranium enrichment facilities for staff that were unfamiliar with this technology. In addition, the initial modeling has been completed, which estimates depths for deposited decay products within the centrifuge walls. Additional modeling is underway to estimate more accurately the growth rate of the UF$_6$ corrosion/passivation layer on the surface of centrifuge for all of the materials of interest. Having a good prediction of the corrosion/passivation layer growth rate will help the interpretation of the surface analysis. By estimating the growth rate, we can determine the length of the operation by measuring the thickness of the corrosion layer.

Samples of various materials of interest have been fabricated to prototypic conditions and exposed to various enrichments of UF$_6$ for surface and chemical analysis. These samples provide the ability for develop a methodology that can be applied to actual hardware. This allows the project to determine which measurement technique or combinations of techniques provide the information needed to determine the characteristics of the uranium enrichment facility. Initial measurements have been made with SEM, XPS, and TOF–SIMS. Chemical etching and mass-spec analysis is planned for the start of FY 2013.

During FY 2013, we will maintain the modeling effort for a uranium enrichment facility, continue refining measurements and data interpretation techniques, and receive and analyze components from an operating enrichment facility.

Physics



Absolute Gas Counting Measurement Techniques

Richard M. Williams

This project aims to improve significantly the uncertainty in radiation measurements of very low activity gas samples. With these enhancements, scientific endeavors ranging from radioisotope dating of environmental samples to nuclear explosion monitoring will stand to benefit.

Low-level radiation measurements are extremely difficult and complex due to the ever present background radiation. To suppress this background, PNNL has developed a unique method to produce ultra-pure copper to fabricate detectors which possess almost no naturally occurring radioactive elements. In addition, PNNL has recently constructed a shallow underground counting facility, which naturally shields some of the cosmic ray background. This project leverages these two existing capabilities and adds a novel counting method to yield a unique, one-of-kind measurement capability.

The objective of our project is to develop a technique to measure the level of radioactivity of gas samples without the need for calibration of the system with reference standards that are often not available, very difficult to obtain, and cost prohibitive to produce. Only a handful of laboratories around the world employ the technique that we are developing here – a process referred to as length-compensated proportional counting – but no other facilities are focused on the same low-level measurements that we are attempting at PNNL.

PNNL-fabricated set of unequal length proportional counters for use in making absolute specific activity measurements of low-level radioactive gas samples.

Our efforts have been organized into a 3-year time frame that began in FY 2012. During this first year of the project, significant progress was made in developing an ultra-low background, absolute-counting measurement capability. Specifically, two different sets of proportional counters (or detectors) were fabricated at PNNL and passed initial characterization tests.

The method of length-compensated proportional counting relies upon the use of a set of proportional counters that are identical, except for their length. The final outcome of the measurement (i.e., the specific activity of the gas sample) is calculated by analyzing the differential count-rates (normalized by the differential gas volumes) from this set of unequal length counters. For this project, two sets of counters were fabricated: the first is a set of three unequal length detectors fabricated using PNNL's ultra-low background (ULB) copper. These ULB counters will be used to make the lowest level measurements in the underground counting facility. In addition, a second set of four detectors was fabricated using high-purity, commercial copper and PNNL's clean assembly techniques. This set is intended for measurements that can be done in one of PNNL's standard, above-ground laboratories.

A key background test has been performed with the ULB counter set. The detectors were filled with standard P10 counting gas (but no radioactive sample) and placed in the shielded counting tomb in the underground laboratory. The background counting rates were on the order of 100 to 200 counts per day (over the full energy spectrum). This outcome sets the conditions for making very low-level measurements with counting times of days or even weeks in the underground facility. Such measurements would not be possible using conventional materials in standard above-ground laboratories, where background count-rates would be in the range of 10,000 to 100,000 counts per day.

During the next year of the project, the measurement methodology will be investigated and the uncertainty of the absolute low-level measurements will be quantified. We will engage with the international radiation metrology community and seek collaborative measurement opportunities to validate the capability that PNNL is developing for basic science applications as well as for nuclear nonproliferation treaty monitoring research and development.

PN12002/2403

Highly Efficient and Cost Effective Gamma Detection Arrays for FRIB

Luke E. Erikson

This project designed a new detector array that would be used in the next generation of nuclear astrophysics experiments to increase understanding of the formation and evolution of the universe.

A new DOE user facility currently under construction at Michigan State University will allow scientists to probe new and exciting topics in nuclear physics. The Facility for Rare Ion Beams (FRIB) is expected to cost approximately $600 million and become fully operational around the year 2020. The higher beam intensities and advanced beam targets will allow scientists to make several first-time measurements of key nuclear reactions. In nearly every case, measurements made at this facility will require the efficient detection of gamma radiation. In fact, several stages of gamma detection will be required for many experiments.

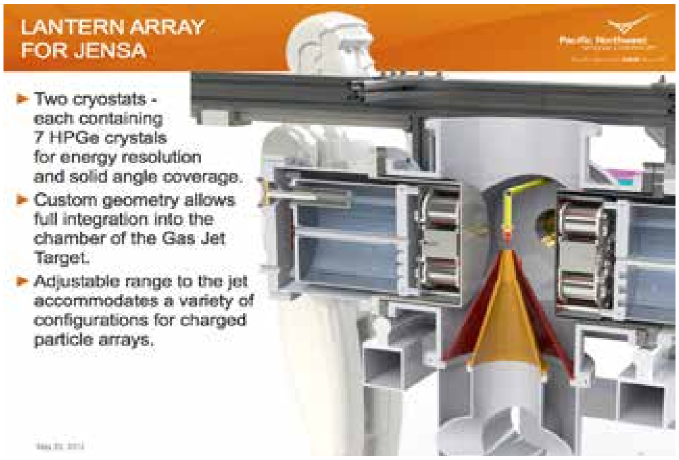
While developing solutions for projects related to national security, PNNL has created a unique infrastructure and expertise in the construction of High-Purity Germanium (HPGe) arrays for gamma detection. One of the approaches used successfully on the MARS, RNLabs, and Majorana projects is the collection of commercially produced HPGe detectors together within a single cryostat. This is a technically challenging approach that has several advantages toward enhancing detection efficiency, meeting unique geometry requirements, and using cost-effective materials. Specifically, this project leverages PNNL's capability in the construction of HPGe arrays into a leadership role in the scientific program that will be undertaken at the FRIB.

Throughout FY 2012, our project has had the following significant accomplishments:

- Completion of initial design for a new 14 crystal HPGe detector array for use at the FRIB and other accelerator facilities. This includes engineering work for mechanical design, crystal mounting, cooling, bias and readout, initial finite element analysis, a rack system for mounting the array at the beamline, initial performance simulations, and an engineering specification/requirements document.
- In May 2012, PNNL hosted a workshop on the Detector Arrays for Nuclear Science. More than 50 leaders from the scientific community from 18 different institutions attended this 2-day event. The agenda focused on PNNL's capabilities in detector research and development. This resulted in a packed schedule of plenary talks and breakout sessions.
- We performed maintenance operations on the second MARS cryostat. In its original configuration, this detector array had 9 of 14 crystals operating. At this time, all 14 crystals are operational (although with three under biased). Unfortunately, this process introduced electrical noise into half of the array, so additional work will be required before the system is ready for deployment.
- Through community outreach, we arranged for the existing MARS array to be included in a nuclear astrophysics experiment at TRIUMF during FY 2013. This experiment will study the ^{20}Ne(p,g)^{21}Na reaction rate, which is relevant to the manner nuclei are formed during stellar nova and is an excellent opportunity to demonstrate PNNL's approach to HPGe detector arrays and their use in this community.
- As part of this project, PNNL is now a member of the JENSA (gas jet target), SECAR (mass separator), and RDS (decay station) collaborations for FRIB.

The primary technical accomplishment is the advanced state of the detector array design. This process was greatly accelerated by extensive reuse of design work for national security clients. For example, the crystal platter and mounts were taken directly from RNLabs, while the integrated crysostat cooling system was inspired by the MARS design.

The present design offers excellent integration into the gas jet target array under construction for FRIB. By taking advantage of the large vacuum chamber of the gas jet target, the detector array provides excellent efficiency for detection and high resolution to increase the signal to noise ratio. The system is designed to be flexible and can translate to accommodate a wide variety of other detectors such as charged particle arrays.



LANTERN ARRAY FOR JENSA

- Two cryostats - each containing 7 HPGe crystals for energy resolution and solid angle coverage.
- Custom geometry allows full integration into the chamber of the Gas Jet Target.
- Adjustable range to the jet accommodates a variety of configurations for charged particle arrays.

Summary of JENSA gas jet target.

PN12038/2439

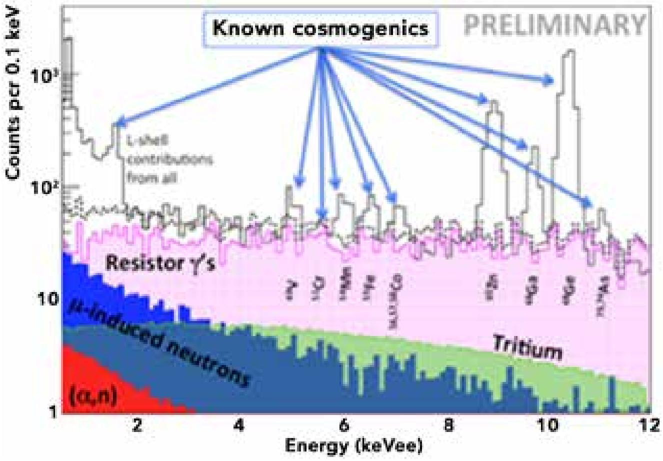
Low Energy Threshold Germanium Detectors and Science

John L. Orrell

This project is developing a low-capacitance, low-background cryostat for germanium detectors for use in ultra-sensitive radiation measurements made in ultra-low-background environments at underground locations. This project also generated a background model for a dark matter experiment searching for a signature of radiation-interaction events induced by dark matter particles.

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. The gravitational effects appear in deviations from uniform intensity of cosmic microwave background radiation, galactic clustering, gravitational lensing, and the rotation of galaxies. The leading theoretical candidate for these gravitational effects is the presence of a weakly interacting massive particle 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 only know and understand a small fraction of the matter composing 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.



GEANT-4 simulation of expected continuum backgrounds for the CoGeNT detector.

In the previous year, we designed, fabricated, and assembled a next-generation low-capacitance, low-background cryostat for ultra-low-energy threshold germanium gamma-ray spectrometers such as is used in the CoGeNT dark matter experiment. The mechanical and thermal design of the custom copper cryostat and cross-arm is based on PNNL's long experience building ultra-low background radiation measurement instruments for applied research and basic science. A mixture of OFHC copper and PNNL's ultra-pure electroformed copper is used in the cryostat construction. The choice of material is primarily driven by fabrication considerations; nevertheless, the background due to ubiquitous U/Th-chain isotopes should be reduced relative to that of the CoGeNT detector cryostat, the design and initial assembly of which are shown.

Left: C4 cryostat design and cut-away view of the interior, showing the low-capacitance mount. Right: Prototype cryostat undergoing vacuum testing in the PNNL shallow underground laboratory cleanroom.

Additionally, we investigated the expected backgrounds of the CoGeNT detector through GEANT-4 simulations. The figure shows results of this simulation effort overlaid with the CoGeNT data. The development of this background model for the CoGeNT experiment is important for understanding if the rising excess of events seen below an energy of 2 keVee is due to known radioactive backgrounds or potentially from the sought after dark matter interactions. The nuclear recoil reactions from dark matter events in such a detector are expected to have an upturn as seen in the CoGeNT data. However, assigning this excess of events to the detection of dark matter is fraught with the danger of both known and unknown backgrounds. Publication of this background model is an important step is demonstrating the capability of CoGeNT-like detectors for dark matter research.

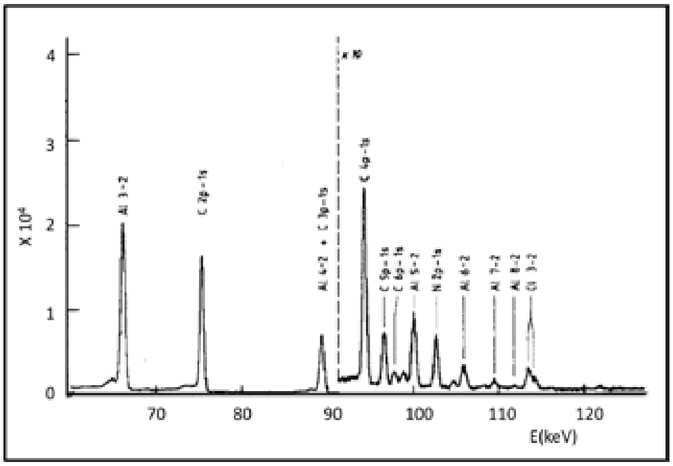
Mu2e September Beam Test

David M. Asner

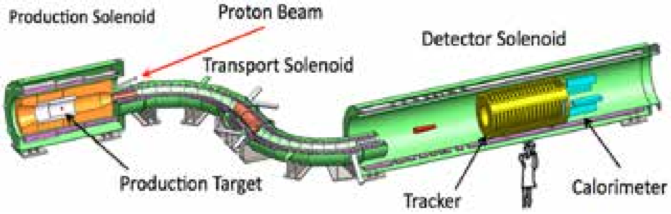
This project prepares a PNNL germanium gamma-ray detector for measurements in a beam test at TRIUMF. The goal is to provide proof-of-concept measurements of muonic X-rays from the stopping target. The project will initiate the effort to simulate detector response and model the overall particle flux at the stopping target monitor location.

The Mu2e collaboration proposed a new facility to study charged lepton flavor violation using the existing DOE investment in the Fermilab accelerator complex. Specifically, Mu2e proposes to measure the ratio of the rate of the neutrinoless, coherent conversion of muons into electrons in the field of a nucleus relative to the rate of ordinary muon capture on the nucleus. The conversion process is an example of charged lepton flavor violation, a process that has never been observed experimentally.

To determine the number of muons captured in the stopping target, the characteristic X-ray spectrum generated by the formation of muonic atoms will be measured with a high-purity germanium crystal detector. Due to high incoming muon flux, the Mu2e environment will potentially contain high rates of neutrons from atomic disassociation in the target. These neutrons can generate defects in the germanium lattice and degrade detector performance. In addition, electrons generated and transported with the muons will create bursts of photons as they interact with the target. The large number of photons generated will potentially blind the detector to the muonic capture X-ray spectrum. Despite these challenges, high-purity germanium is still the detector of choice for high-resolution X-ray and gamma-ray spectroscopy measurements.



Lyman X-ray spectrum from muon capture by ^{27}Al.



The Mu2e detector as currently envisioned. The stopping target monitor will be located at the end of the detector solenoid at far right.

This project includes development of the detector data acquisition system in advance of the beam test at TRIUMF where data will be collected at the muon stopping target in several configurations including muon beam on with and without stopping target and background data while the muon beam is off. Once data are collected, they will be analyzed to identify X-rays from the stopping target and other potential sources from the beam and room backgrounds. The resulting measurements of rate and resolution will be used in further research and development of the stopping target monitor and will be presented to the greater Mu2e collaboration. As a parallel task at PNNL, integration of the germanium gamma-ray detector into the Mu2e detector simulation and the simulation of the particle flux in the vicinity of the stopping target monitor will be initiated.

Additional activities during FY 2012 included three PNNL staff participating in a week-long software and simulation workshop at Fermilab. Both the effort to model the germanium gamma-ray detector in the Mu2e detector simulation and modeling the particle flux near the stopping target have been initiated. A XIA PIXIE-based data acquisition system utilizing PNNL-developed software with data output into the high energy physics standard ROOT format for subsequent data analysis with the ROOT toolkit was also developed. Along with PNNL, scientists from Osaka University, the University of Washington, Fermilab, and TRIUMF will operate additional detectors at the TRIUMF beam test. Planning for the beam test and coordination of the data acquisition for the various detector systems was performed in collaboration with the other participants.

Due to technical problems with a superconducting solenoid on the TRIUMF M9B beamline, the September beam test was cancelled and rescheduled for November. Finally, a proposal has been submitted to DOE to support PNNL participation in the Mu2e experiment at Fermilab.

PN12049/2450

Nuclear Astrophysics Measurements using High-efficiency HPGe Arrays

Robert Runkle

This project uses a PNNL-constructed state-of-the-art detector array to measure a nuclear reaction, which is important to understanding the evolution of normal matter in the universe.

Precise knowledge of reaction rates are key to understanding how stars age. For many stars, the $^{14}N(p,g)^{15}O$ reaction is a bottleneck that limits energy production and therefore plays an important role in the star's evolution. However, the low rate also makes the reaction difficult to measure. Despite several attempts during the last couple of decades, experiments have suffered from low statistics and backgrounds that make data analysis difficult.

The goal of this project is to improve substantially our knowledge of the $^{14}N(p,g)^{15}O$ reaction while demonstrating the capabilities of PNNL's MARS array. The combination of segmentation, detection efficiency, and high resolution gives the MARS system several advantages over typical laboratory detectors. For this reason, we viewed this project as an opportunity to leverage our successes in the national security domain to address a basic research need.

Our project hinged on successful university and laboratory collaborations. The measurement of these reaction rates requires access to a suitable accelerator facility and support staff. One of the few locations in the world equipped to conduct the experiment is the Laboratory for Experimental Nuclear Astrophysics (LENA) at the Triangle Universities Nuclear Laboratory (TUNL).

The MARS detector array integrated into the LENA beamline at TUNL in July 2012.

In collaboration with University of North Carolina (UNC), local support was obtained for operating MARS within the LENA target station during summer 2012, and preparations began for an experiment.

For this measurement, one advantage of the MARS array over a typical laboratory system is the segmented design consisting of 14 high purity germanium (HPGe) detectors. The $^{14}N(p,g)^{15}O$ reaction tends to produce multiple gamma rays per reaction, which can make recognition of individual gammas difficult. This problem increases as larger detectors are used and/or when placed in closer proximity to the reaction. However, a segmented detector reduces the likelihood of these summing effects and also allows for alternative analysis techniques such as anti-coincidence counting.

By mid FY 2012, PNNL staff relocated MARS to LENA by ground transportation and integrated the system into the beamline for the experiment. During the following week, PNNL staff scientists worked with students and faculty at LENA to produce approximately 6 GB of data from the MARS detector while measuring the $^{14}N(p,g)^{15}O$ reaction. The MARS system ran smoothly throughout the experiment.

This represents the first time that a high-efficiency HPGe array produced at PNNL has been used for a nuclear astrophysical experiment. For this reason, we expect two publications to be produced from this effort: a technical paper discussing the value of the PNNL approach to high efficiency arrays, and a journal article to report the results of the reaction rate measurement.

The MARS detector system was successfully deployed at LENA and used to measure a nuclear reaction important to humankind's understanding of the universe. During the experiment, accelerators at LENA delivered approximately 15 Coulombs of protons on a Ta target implanted with 0.5 Coulombs of ^{14}N ions.

Analysis of the data is being conducted at both PNNL and UNC. Preliminary results show that the $^{14}N(p,g)^{15}O$ was detected with enough accuracy to produce a publishable result. Additionally, the segmented nature of the MARS array has had beneficial effects for example when operated in the anti-coincidence mode to reduce backgrounds.

PN12058/2459

Search for New Physics at the Intensity Frontier

David M. Asner

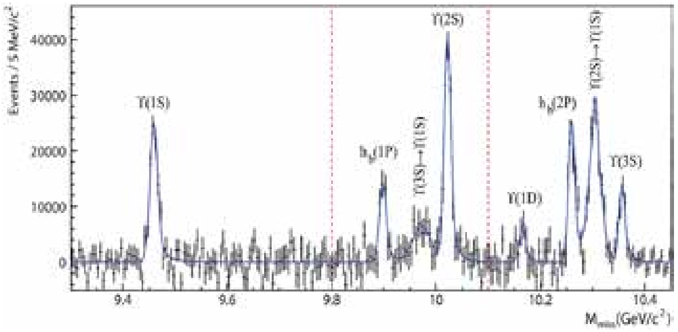
This project analyzes the world's largest sample of heavy quark decays recorded by the Belle detector at the KEK Laboratory in Tsukuba, Japan. The goals are to discover and characterize the properties of exotic bound states of matter and anti-matter. This project will also lay the foundation for leadership in the physics program at the upgraded facility Belle II/ SuperKEKB.

Discovery and characterization of the properties of exotic states of matter recorded by the Belle detector are the objectives of this research project. The Belle detector, operated at the asymmetric electron-positron collider KEKB from 1999 to 2010, accumulated the world's largest data sample for the study of B mesons (subatomic particles containing one heavy bottom quark and a light anti-matter quark) and Bottomonia (bound states between a heavy bottom quark and a heavy anti-matter bottom quark). Bottomonia states were first observed about 30 years ago. However, there remain areas in which knowledge of these systems needs improvement, including anticipated but unobserved states of matter. Specifically, bottomonia spectroscopy is generally regarded as a key source of information necessary for the development of the understanding of the quantum theory describing the strong interaction that holds atomic nuclei together.

A goal of this project is to refine our understanding by making new and more precise measurements of the parameters of the bottomonia states, their decays, and their transitions. The expected results of this endeavor provide important benchmarks for a variety of theoretical approaches. This project is seeding the initial collaboration between PNNL and the international Belle research team, which consists of a collaboration of 300 physicists across four continents.

At the conclusion of FY 2012, this project has had the following significant accomplishments.

- We made a discovery of two exotic states of matter collectively referred to as Bottomonium p-wave singlets and named h_b(1P) and h_b(2P), respectively. These results were presented at the prestigious international conference *Rencontres de Moriond* in La Thuile, Italy and published in *Physical Review Letters*. Thus far, this journal publication has been cited 50 times.



Analysis of the Belle data sample reveals six bound states of a bottom quark and its anti-particle including the previously h_b(1P) and h_b(2P).

- We encountered a first observation of radiative transitions from p-wave to the s-wave singlet states denoted as η_b(1S) and η_b(2S). This work includes the most precise measurements of the properties η_b(1S): the Bottomonium ground state. These results were presented at the *11th Conference on the Intersection of Particle and Nuclear Physics* and submitted for publication.
- We performed searches for new phenomena in D mesons (bound states of a charm quark and a light antimatter quark) and are a focus of planned FY 2013 work. Two publications – one update of an article in collaboration with Cornell University from *Physical Review D* and two mini-reviews in the biennial *Review of Particle Physics* – during FY 2012 lay the groundwork for that effort.

This project has enabled PNNL to build a reputation for scientific excellence through the discovery and elucidation of bottomonium states in FY 2012. Next year, the focus will shift to the search for new phenomena in B and D meson decays. A 50-fold increase in data volume is anticipated at the upgraded Belle II detector. This project will lay the foundation for PNNL leadership in the Belle II physics program.

In FY 2013, several conference talks and three specific publications are planned: one report in collaboration with Luther College on the study of the χ_b(3P) bottomonium state, a second study on matter anti-matter oscillations with D mesons, and finally an article in collaboration with Yonsei University in South Korea on a search for rare and forbidden decays of B mesons.

Ultra-Precise Electron Spectroscopy to Measure the Neutrino Mass

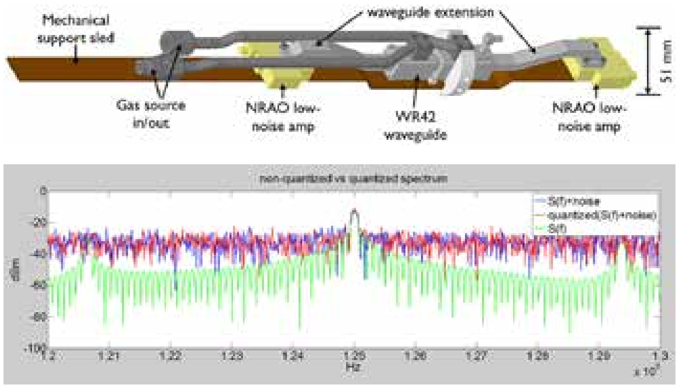
Brent A. VanDevender

This project is developing a fundamentally new spectroscopy technique to be applied in the search for the absolute mass of the neutrino.

Neutrino mass has far-reaching implications from theories beyond the standard model of particle physics to the evolution of large-scale structures in the universe. As DOE rates the measuring of neutrino mass as one of its top priorities in basic nuclear science, we are developing a new technique for the spectroscopy of medium-energy (1–100 keV) electrons based on the detection of cyclotron radiation emitted by magnetically trapped electrons. The energy of a trapped electron is encoded in the frequency of the radiation. Because frequencies can be measured with extreme precision, our method promises energy resolution superior to existing techniques. The goal is to measure the mass m of the neutrino involved in tritium beta decay by observing a small reduction in electron energy E that can be attributed to neutrino mass by Einstein's relation of $E = mc^2$. Experiments based on existing techniques have reached their ultimate neutrino mass sensitivity and may still not be sufficient to weigh the neutrino, which could be up to 100 times lighter still.

Scientists and engineers at PNNL have formed the Project 8 collaboration with colleagues from the University of Washington (UW) Center for Experimental Nuclear Physics and Astrophysics, Massachusetts Institute of Technology, University of California-Santa Barbara, and the California Institute of Technology to develop the technique and use it to measure the mass of the neutrino. Our immediate goal is to demonstrate the ability to detect the cyclotron radiation from individual trapped electrons and reconstruct an energy spectrum with a prototype experiment at UW. The prototype demonstration will be made with ^{83m}Kr, a radioactive gas that emits electrons with similar energies as tritium but in a much more simple spectrum that will allow us to discern instrumental effects from true spectral features.

PNNL manufactures the ^{83m}Kr sources for the prototype. Project 8 needs a strong source and our resident radiochemistry experts are able to do this safely and precisely, and ^{83m}Kr is widely used as a calibration standard. While there are several source production recipes to be found in the literature, our case is so far unique and requires original methods to prepare sources for use in ultra-high vacuum environments. PNNL made one source in FY 2012 and has obtained material to replenish that source early in FY 2013.



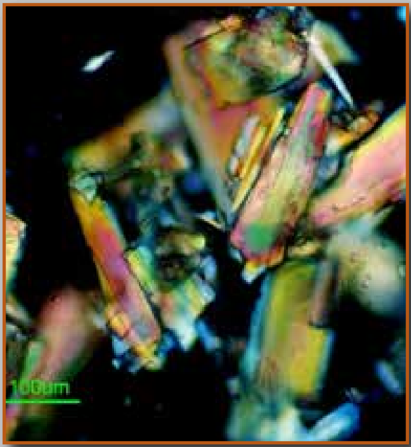
The Project 8 prototype apparatus with source gas decays in the WR42 waveguide. Cyclotron radiation from resulting trapped electrons propagates down the waveguide to low-noise amplifiers in either direction that prepare the signals for collection by a data acquisition system. The plot is the expected frequency spectrum of signal and noise.

The expected cyclotron signal is in the microwave frequency range. PNNL provides the primary electrical engineering support for microwave receiver design and analysis. Initial concepts for Project 8 were based on antenna receivers. These were shown to be inferior to concepts based on waveguides and/or resonant cavities. A waveguide design was chosen for the current prototype and confidence that it will be successful is based largely on a detailed PNNL simulation and analysis of the full signal chain from propagation in the waveguide through the receiver electronics to collection in the data acquisition system.

The waveguide prototype will begin operating in late FY 2012 and is expected to generate its first result during FY 2013. An article regarding the observation of individual trapped electrons by detection of their cyclotron radiation will be submitted for publication. In addition, a companion article about the technique and apparatus will be submitted to *Nuclear Instruments and Methods A*. The next result will be a measured energy spectrum of ^{83m}Kr conversion electrons based on a larger number of observations and submitted to *Physics Review Letters*.

In parallel with support of the waveguide prototype experiment in FY 2013, PNNL will work on the design and implementation of a prototype based on resonant cavities. A feasible cavity geometry was already identified in FY 2012. Ultimately, the approach that most readily scales for the much larger experiment required to measure neutrino mass with tritium will be chosen and proposed to the DOE Office of Nuclear Physics.

ON THE COVER:



Using expertise in material nuclear forensics, PNNL scientists and engineers are developing cutting-edge signature discovery tools related to the nuclear fuel cycle. This image of thorium nitrate and uranyl sulfate crystals was obtained from a Nikon 400 POL polarized light microscope (PLM) with cross-polars. The PLM provides unique insight into materials and enables rapid screening of unknowns. The cross-polars image of uranyl sulfate shows large 0.5-millimeter crystals exhibiting a wealth of interference colors. Contrasts in the images are due to thickness variations across the crystal, much like the interference colors from an oil slick on water. This work was jointly funded by NA-20 and National Technical Nuclear Forensics Center (NTNFC), and supports the Laboratory's major initiative in Signature Discovery and Exploitation for Threat Detection and Reduction. PNNL scientists Leah Arrigo and Crystal Rutherford contributed to the project, which is managed by Jon Schwantes. *This image was provided by PNNL scientist Edgar Buck.*

A metal-organic framework (MOF) composed of zinc nitrate and 2,5-dihydroxy terephthalic acid was imaged at 10,000-times magnification as part of a study to understand how nanoporous frameworks can be created and modified to improve gas capture properties. The MOF is part of a new series of materials developed by PNNL that have tiny "cages" that can be used to trap carbon dioxide. The crystals in the cages have a diameter of about 25 nanometers. The cages themselves consist of metal ions linked together with organic ligands forming a porous network that traps gas molecules. The unique molecules have two to three times the capacity for carbon dioxide uptake as conventional solvents and appear to have an extremely high preference for carbon dioxide over other gasses. This research was funded by BES, and supports the Laboratory's major initiative in Coupling Earth and Energy Systems for Sustainability. This image (in false color) was captured using a focused ion beam scanning electron microscope at the Environmental Molecular Sciences Laboratory (EMSL), a DOE national scientific user facility. *Image provided by EMSL's Bruce Arey and PNNL's Carlos A. Fernandez and Praveen Thallapally.*

Microbe-mineral and -metal interactions represent a major intersection between the biosphere and geosphere but require high-resolution imaging and analytical tools for investigating microscale associations. Electron microscopy has been used extensively at PNNL for geomicrobial investigations such as the controlled exposure of model organism *Shewanella* to environmentally relevant metals and radionuclides to understand how microbes carry out complex biogeochemical processes. At EMSL, scientists are using the state-of-the-art instrumentation and expertise in electron microscopy imaging and analyses for research of the effects of the interactions of microbes with the soil environment. Shown here is a scanning electron micrograph of *Shewanella putrefaciens* CN-32 cells in certain conditions that induce cells flocculation. CN-32 is a metal-reducing bacteria important for stabilization of metals in the environment. This work was funded by BER, and supports the Laboratory's major initiative in Accelerating Innovation and Discovery and Transforming the Conduct of Science in EMSL. *This research was carried out in PNNL's Microbiology group led by Jim Fredrickson, the image was provided by EMSL scientist Alice Dohnalkova.*

2012 Annual Report

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