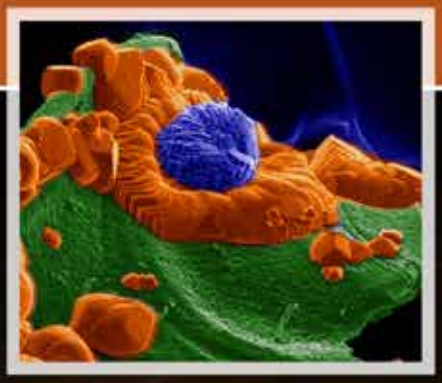
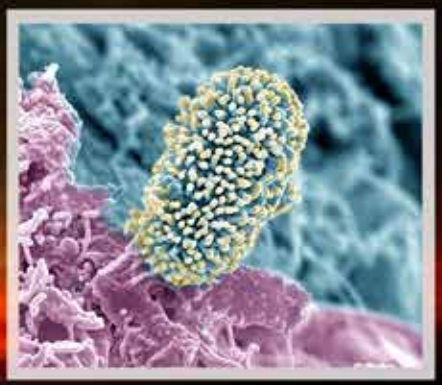
2015 Annual Report

Laboratory Directed Research & Development
at Pacific Northwest National Laboratory

PACIFIC NORTHWEST 50 1965–2015 Years NATIONAL LABORATORY





DISCOVERY *in Action*

Pacific Northwest
NATIONAL LABORATORY

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

U.S. DEPARTMENT OF
ENERGY

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

PNNL-25278

Laboratory Directed Research and Development Annual Report

Fiscal Year 2015

March 2016

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

Pacific Northwest National Laboratory
Richland, Washington 99352

Contents

Laboratory Director's Message vii

Advanced Sensors and Instrumentation

A Self-powered Acoustic Transmitter for Aquatic Animals 1
Alpha Coincidence Techniques for Actinide Assay 2
Combined Microscale ^{13}C and ^{18}O Measurements at Cutting-Edge Sensitivities and Spatial Resolution 3
Creating a Gas Phase Chemistry Workbench by Performing Manipulations in Efficient Ion Traps 5
Development of an Ultra-Small Volume Detection and Sample Delivery System for Exploring Microscale Heterogeneity with NMR 6
Development of Coded Aperture Compressive Sensing Acquisition in Environment Transmission Electron Microscope . 7
EUV Laser Ionization Mass Spectroscopy 8
Free Form Millimeter-Wave Imaging 9
Hybrid Microchip/Capillary Electrophoresis Platform for Rapid, Ultrasensitive Bioanalysis 10
Low Background Light Sensitive Photo-Diode Array for Scintillator Readout 11
Low Background Liquid Scinitillation Counter 12
Mössbauer Spectral Imaging 13
Platform for Large-Scale Determination of Protein-Ligand Binding 14
Single-Step 2-D Ion Mobility Separations Technology 16
Universal Liquid TEM Microfluidic Cells Based on SALVI for Predicative Materials 17
Vapor Detection of Illicit Substances in an Atmospheric Flow Tube Mass Spectrometer 19

Biological Sciences

Aperture 21
Biological Threat Signatures for *Bacillus anthracis* 23
Chromatin Activity Precipitation (TIP) 24
Cultivation-independent Untangling of Microbial Gene Regulation Networks 25
Developing a Next Generation Biogeochemical Module for Earth System Models 27
Dissection and Deciphering of the Soil Microbiome 28
Drugs of Abuse Retention and Degradation in Environmental Biofilms 30
Exploring and Engineering Phototrophic-Heterotrophic Partnerships 31
Global Forensic Chemical Exposure Assessment for the Environmental Exposome 32
Imaging and Monitoring the Initial Stages of Biofilm Formation 34
Impact of Environmental Stressors on Complex Biological Systems 35
Increasing Annual Biomass Productivity Through Development of Cold Tolerance in Algae 36
Microbial Community Dynamics and Plant Phenomics with Single-Cell Gene Expression and Imaging Mass Spectrometry 38
Microbiome Models Across Scales - From Metabolism to Succession: A Framework for Modeling, Simulation and Theory Development for Microbial Ecology 39
Microbiome Responses to Hydrologic Regime Shifts and Subsequent Alteration to Ecosystem Function 41
Microbiome-Exposome Interactions 42
Multi-Scale Processes Controlling Spatial Variation in Greenhouse Gas Emissions in a Subarctic Watershed 44
Optofluidics and Microfluidics for Exploring Biofuel Production at the Single Cell and Molecule Levels 45
Rapid Viability Assays for Biothreat Event Characterization 46
RhizoControl: Does the Rhizospheric Microbiome Influence the Plant Metabotype? A Plant Gnotobiotics Approach . 47
Rhizosphere Underground: Unraveling the Role of Microbes in Stabilizing Carbon Pools in Soils 49
Signatures of Environmental Perturbation – Microbial Community and Organic Matter Resilience 50
Statistical Integration of Omics Data from Microbiomes 51
Structure and Dynamics of Biological Systems 52
Understanding Cellular Communication and Controlling Directional Flow of Nutrients 53

Chemistry

Bio-Inspired Actinides Recognition for Separation Science . . . 55
Bio-inspired Selective Conversion of Methane to Methanol . . . 56
Biomass-Derived Acrylonitrile for Carbon Fiber Production . . . 57
Climate-Related Chemistry of Internally Mixed Atmospheric Particles . . . 58
Development of a Novel Microscopy Platform for Fundamental Studies of Ice Nucleation on Atmospheric Particles . . . 59
Dynamics of Supported Noble Metal Nanoparticles in the Presence of Oxidizing Environment: Application of Compressive Sensing in ETEM . . . 61
Electrocatalytic Reduction of Phenols and Ethers . . . 63
Fundamental Understanding of Nucleation Processes to Assess Solution Stability and Phase Growth and Genesis . . . 65
Localized Surface Plasmon Resonance Spectroscopy, Microscopy, and Sensing . . . 67
Making, Measuring, and Modeling Materials for Quantum Computing . . . 69
Marine Radiochemistry: First Th-231 Measurements in Seawater for Tracing Rapid Particle Dynamics . . . 71
Molecular Fingerprint of ANFO Detonation . . . 73
Novel Alloy Nanoparticle Materials for Catalysis and Energy Storage . . . 74
Predictive Understanding of Self-Assembly: Particle-Mediated Growth . . . 76
Scalable Synthesis of Spinel Stabilized Metal Catalysts . . . 77
Sequence-Defined Polymers Based on a New Backbone Architecture . . . 78
Simultaneous Electrochemical and Nuclear Magnetic Resonance Techniques for the Study of Electrochemically Active Biofilms . . . 79
Sub-Surface Catalytic Conversion of Oil Shale Kerogen into Shale Oil for Enhanced Oil Recovery . . . 80
Thermal- and Electro-Catalytic Routes to Conversion of Phenols to Fuels and Chemicals . . . 81

Earth and Space Sciences

Assessment of Geophysical Tracers for Characterization of Natural and Stimulated Fracture Networks . . . 84
Coupling the Spectral-bin Cloud Microphysics with Chemistry/Aerosol in WRF-Chem Framework . . . 86
Determining Groundwater Residence Time Through Ultra-Low Measurements of ^{39}Ar and Other Radiotracers . . . 88
Development of Integrated Modeling Framework to Quantify Strong Interdependencies and Vulnerabilities Between Water and Energy in the Western Interconnection . . . 90
Enhanced Sediment Geochronology Achieved Using Ultra-Low Background Materials and Ultra-Sensitive Detection Capability . . . 91
How Do Non-linear Microbial Processes Lead to Linear Ecosystem Fluxes? . . . 94
Identifying Cloud Phase States from Multiple Remote Sensing Observations . . . 95
Measuring and Modeling the Climatic Effects of Brown Carbon Atmospheric Aerosols: Developing an Integrated Capability . . . 96
Nonstationary Climate Considerations - Climate and Hydrology . . . 98
Nonstationary Climate Considerations - Floods and Consequences . . . 100
Numerically Robust Climate Simulation Through Improved Interaction Between Model Components . . . 102
Quantifying Carbon Fluxes and Underlying Mechanisms Using Multiple Data Sets with a Joint Land-Atmosphere Ensemble Kalman Filter Data Assimilation System . . . 103
Regional-Scale Measurement and Modeling of Biogenic Organic Fluxes: Bridging the Gap Between Process Studies and Climate Models . . . 105
Simultaneous ^{14}C and T Dating of Environmental Organic Matter . . . 106
Using Multiple-Degree-of-Freedom Feedback to Auto-Tune Climate Models . . . 108

Energy Supply and Use

Advanced Visual Analytic for the Power Grid . . . 110
Agent-Based Testbed for Complex Building Control Systems . . . 112
Aggregate Load Modeling and Control for Power Grid Regulation Services . . . 113
Complex Systems Control Testbed . . . 114
Decision Theory for Incentive Compatible Mechanism Design . . . 115
Development of a Combined High-Pressure, High-Temperature NMR Rotor Capability . . . 117

Distributed Control of Large-Scale Complex Systems 119
Electrolytes Enabling Low Temperature Battery Operation. 120
Experimental Management for Controls of Complex Systems Test Bed 121
GridOPTICS. 122
Human Factors Issues for Lighting Systems 124
Impacts of Communication Network on Distributed Control. 126
Implementation of Extremely Large Scale Building Energy Simulation Infrastructure 128
Integration and Demonstration of Co-simulation Platform in the CCSI Test Bed 129
Integration and Demonstration of Scalable Power System Simulation for CCSI Test Bed 130
Market Design Analysis Tool 131
Multidimensional Membrane Theory to Predict Power System Oscillations 132
Operations and Planning Fusion 133
Resilience in Large-Scale Distributed Control Systems 134
Transactive Control of Commercial Buildings for Demand Response 135

Engineering and Manufacturing Processes

Composite Turbines for Small Hydro 138
Graphene Oxide Based Structured Laminar Membranes 139
Interfacial Engineering: A Theory Based Approach to Join Dissimilar Materials 141

Materials Science and Technology

Atomistic View of Solid-Liquid Interfaces Using *In situ* X-ray Probes 143
Bridging Length Scales in Complex Oxides: From Point Defects to Defect Superstructures 145
Controlled Synthesis of MOFs and Core-Shell MOF Composites. 147
Developing Next-Generation Multimodal Chemical Imaging Capability by Combining STEM/APT/STXM/HIM 148
Development of Hierarchical Porous Structured Materials for Energy Storage Applications 150
Development of Viologen Based Ultra-low Cost and High Performance Aqueous Redox Flow Batteries 152
Directed Mesoscale Synthesis of Tunnel Structured Materials for Energy Applications 153
Enabling Sodium Batteries with Advanced Electrolytes 155
Fundamental Mechanisms of Nucleation and Growth of Particles in Solution 156
High Aspect Ratio Functional Composites for Thermal Optical Applications. 157
High Information Content Polymers and Their Assembly into Structural Motifs. 158
High Resolution and 3D Imaging of Nanomaterials 159
Highly Dispersible, Thermally Stable Core/Shell Proppants for Subsurface Stimulation 160
Improving Magnetoelectric Coupling in Novel Single-Phase Multiferroic Thin Films of the $MTiO_3$ (M = Fe, Mn, Ni ...) Family 162
Improving the Performance of Li-Air and Li-S Batteries Using Polymeric and Metallic Nanomaterials 164
Inorganic Composites for Tc Alternative Waste Forms 166
Membrane Reactor-Enabled Manufacturing Processes of Nano-Metal Particles 168
Meso-Scale Science and Technology: Manufacturing of Nanostructured Soft Magnetic Materials. 169
Modeling the Interfacial Effects, Partitioning, and Production Routes of Epsilon Particles in Uranium Oxide 171
Nanocomposite Particle Synthesis Using Switchable Ionic Liquids. 172
Novel CO_2-Selective Polymer/Double Salt Composite Membranes for Continuous CO_2 Removal from Warm Syngas . . .174
Observing and Quantification of the Initial Stages of Nucleation and Growth in Liquids 175
Optical Properties Modification in Complex Oxide Epitaxial Films via Alloy Formation 176
Optically Resonant Subwavelength Films for Tags and Seals 177
Optically Stimulated Luminescence Data Storage 178
Oxygen Sensors by Plastic Impregnation Using Solvent Immersion Methods 179
Probing Structure-Property Relationship of Energy Storage Materials Using ***Ex Situ*** and ***In Situ*** Dynamic Microscopy and Spectroscopy with High Spatial and Fast Temporal Resolution 180
Rheoreversible CO_2-Reactive Hydraulic Fracturing Fluids for Unconventional (Tight) Oil Production 182

Robust Hierarchical Zeolite Frameworks 184
Scale-up of New Chemistry Batteries for Transportation and Stationary Applications, Material Synthesis and Pouch Cell Development. 185
Soil Organic Carbon/Mineral Association and Aggregation Processes 187
Sub-wavelength Paint with Tailored Visible and Infrared Light Scattering for Energy Applications 188
Tailored Electrolytes for Lithium-Polysulfide (Li/PS) Redox Flow Batteries 189
Ultra-Low Background Polymers for Structural Applications in Radiation Detectors 191

Mathematics and Computing Sciences

A Population Based Approach for Hypothesis Generation and Control 193
Analytic Framework: Signature Discovery Workbench 194
Analytics Integration and Validation Framework. 195
Applying the Active Data Canvas to Biological Sciences 196
Characterization of Anonymous Peer-to-Peer Networks 197
Cognitive Depletion in Streaming Environments 198
Compression Statistics for Analysis of Streaming Data 199
Co-Simulation Platform for Rapid Prototyping of Control Algorithms 200
Cyber Risk Assessment Model (Cyber RAM) 201
Cyber Security Testbed and Dataset Generation 202
Developing Signatures that Relate Fecal Microbiome Characteristics with Gastric Bypass Surgery Outcomes 204
Development of an Computational Image Analysis Tool 206
Digital Currency Graph Forensics to Detect Proliferation Finance Patterns 207
Discovery of Cyber/Physical Qualifiers' Relationship and Relevance to Probabilities of Detection/Non-detection Mitigations 208
Dorci - The Defenders Role in Resilient Cyber Security 209
Estimation of Battery State of Health Using Utility and Literature Data 210
Exploring Multilevel Numerical Methods in Continuous and Discrete Systems for Extreme-scale Computing 211
Family of Resilience Metrics for Cyber Security Operations 213
Fishing for Features: Discovering Signatures When the Underlying Phenomenon is Poorly Understood 214
High-Level Modeling Specification for Simulation of Control Systems 216
Image Analysis using Active Learning on Shape and Texture Features 217
Integrated Adaptive Resilient Asymmetric Data Security 219
Kritikos: Identifying Cyber Assets and Assessing Criticality in Terms of Business Processes 220
Leveraging Power Grid Contingency Analysis Techniques For More Resilient Cyber Networks 221
M&Ms4Graphs: A Multi-Scale, Multi-Dimensional Graph Analytics Framework for Cyber Security 222
Module Integration Interface for Resilient Cyber Systems (MiiRCS). 223
Multiscale Modeling and Uncertainty Quantification for Complex Non-Linear Systems 224
Network Chimera 226
NOUS: Incremental Maintenance of Knowledge Graphs 227
Online Predictive Analytics on Streaming Data 228
Rendezvous: Optimization and Stochastic Algorithms for Asymmetric Resilient Infrastructure 229
Scalable Feature Extraction and Sampling for Streaming Data Analysis 230
Scalable Hierarchical Validation and Calibration for Robust Distributed Control of Large-scale Complex Systems Under Uncertainty. 232
Scalable High-Level Programming 233
Science of Interaction: Towards Human-Machine Co-Reasoning. 234
Scire: Scientific Process for Validation and Verification 235
Shyre: Streaming Hypothesis Reasoning 237
Signatures of Communities and Change 239
Signatures of Illicit Nuclear Trafficking for Strategic Goods (SINTS) 240

Streaming Data Characterization 242
Theory of Resilience 243
Topological Analysis of Graphs in Cyber Security (TAGs-CS) 245
Towards One Health Disease Surveillance 246
Unmask Signatures of Cell Perturbation Hidden in the Normal Variability Between Cells 247
User-centric Hypothesis Definition 248
Visual Analytics Platform for Large-scale Hierarchical Control System Data 249

Nuclear Science and Engineering

An *In situ* Investigation of Gamma-AlOOH Dissolution under High pH Conditions 251
Atomic Mass Separation for Enhanced Radiation Detection Measurements 253
BazookaSPECT Neutron Imager 254
Correlation of Colloidal Interactions and Macroscopic Rheology in Concentrated Electrolyte Solutions 255
Detection of Production at the Source 257
Development of a PNNL Underground Nuclear Explosion Simulation Tool 258
D-T Neutron Generator Based Standard to Replace ^{252}Cf 259
Feasibility of a Dual-Wavelength, Dual-Scintillation Material Fast Neutron Detector Concept Using Bragg-Peak Peak Detection Physics 260
Gamma-gamma Coincidence Analysis Algorithms 261
Hot Particle Analysis Aided by a State of the Art Focused Ion Beam 262
MANDRAKE 263
Modeling the Long-term Degradation of Spent Nuclear Fuel Dry Cask Canisters 264
Monitoring Diffusion of Actinide Daughters and Granddaughters in Metals for Chronometer Applications 265
Signatures of PuF_4 and Pu Metal Processing 266
Signatures of Underground Explosions (SUE) 267
Solving the Pu-238 Problem. 268
Technologies for Non-intrusive, Unattended Measurement of UF_6 Gas Flow. 269

Physics

Anthropogenic Uranium Detection with X-ray Microscopy 271
Dark Matter Physics 272
Discovering CENNS in MiniCLEAN at Fermilab 273
Laser-ablation Based Multimodal Tool for Nuclear Forensics 274
Modeling Underwater Sound in Coastal Environment to Accelerate Development of Renewable Ocean Energy 275
Resolving the Reactor Neutrino Anomaly by Precision Beta Spectrometry 276

Laboratory Director's Message

For more than fifty years, Pacific Northwest National Laboratory has advanced the frontiers of science and engineering in the service of our nation and the world. We make fundamental discoveries that expand our understanding of the universe and we apply our expertise to some of the world's most challenging problems in energy, the environment and national security.

As a national lab, it is imperative that we steward our scientific and engineering capabilities in support of the Department of Energy's missions and evolving national needs. As part of our annual strategic planning process, we decide where to invest our discretionary R&D funding—looking carefully at where we can deliver transformational S&T, accelerate innovation, develop new partnerships and enhance our core capabilities. One result is an annual portfolio of Laboratory Directed Research and Development projects.

This report summarizes our FY 2015 LDRD portfolio and highlights the breadth and depth of our researchers' creativity and innovation. We are proud to share some of their amazing accomplishments and exciting plans for the future. In so doing, you will gain a sense of the multidisciplinary approach that we take to scientific discovery and problem solving. This report also describes how we conduct our LDRD program, as well as how it aligns with DOE's strategic objectives and adheres to program guidelines.

Thank you for taking the time to learn about our LDRD program. I am confident that you will come away with a deeper appreciation for the value of this program and the terrific talent behind it.

Steven F. Ashby

Dr. Steven Ashby
Director, PNNL

Advanced Sensors and Instrumentation

A Self-powered Acoustic Transmitter for Aquatic Animals

Z. Daniel Deng

This project successfully demonstrated an acoustic transmitter powered solely by the swimming motion of a benchtop robotic fish to expand our capabilities in long-term fish tracking and their migration behavior studies.

Despite many years of research on salmon recovery, there is a lack of information on both Atlantic and Pacific salmon and other fish, across all of their life stages. In addition, other species with long life history such as American eel and lamprey that are likely to be listed under the Endangered Species Act soon will have major impact on hydropower operations. Though there exists an urgent need for a long-life monitoring technology, autonomous electronic (especially micro) devices are limited by the finite energy capacities of their batteries. For example, a small injectable acoustic PNNL-developed micro-transmitter compatible with the Juvenile Salmon Acoustic Telemetry System (JSATS) to track juvenile salmon lasts only 90 days even though its battery accounts for about half of its weight and volume. Therefore, an energy harvesting unit that would scavenge the mechanical energy from the motion of fish swimming could significantly extend the service life of the transmitter or even enable self-sustained micro devices that could operate over the lifetime of the host.

The newly developed injectable JSATS acoustic micro- transmitter by PNNL consumes only a very small amount of power (2–10 micro watts) that is well within the energy production capability of piezoelectric energy harvesters reported in the literature. Therefore, we employed a piezoelectric-based device that could harvest the mechanical energy generated by the swimming motion of the tagged fish to power the transmitter.

This study was conducted in three stages: the selection of the suitable piezoelectric materials for the energy harvesting element; the design of the energy harvesting device; and testing of the self-powered transmitter prototype. We first evaluated different types of piezoelectric materials, which included piezoelectric polymers, ceramics, and composites for optimal energy harvesting performance in this application. Various types of configuration of the energy harvesting elements were also investigated to maximize the amount of harvested energy.

By incorporating a piezoelectric energy harvesting beam and corresponding energy harvesting circuits with the newly developed JSATS injectable tag, two versions of the self-powered transmitter were developed: one with a rechargeable battery and one without. The no-battery design transmits acoustic signals as soon as the energy storage capacitor has accumulated sufficient energy for several transmissions, while the with-battery design stores the harvested energy into a rechargeable battery and maintains a constant transmission at a certain pulse rate interval.

To evaluate the energy harvesting performance of the self-powered transmitter prototypes, we designed and fabricated a benchtop robotic fish using servo motors and silicone, which can mimic the swimming motion of a fish at various tail beat frequencies. We investigated the number of pings (transmissions) that a fully-charged capacitor can produce, the time taken for a fully depleted capacitor to be fully charged by the energy-harvesting element and the minimum pulse rate interval (ping rate) the transmitter can sustain. By implanting the energy harvesting element into the robo fish and operating the fish at 1 Hz tail beat frequency, we successfully demonstrated that an acoustic transmitter that can transmit acoustic signals at a source level of 150.1 dB at a sustainable ping rate of 2 seconds.

Work related to this project has been published in both *Scientific Reports* and *Applied Physics Reviews*. In addition, other funding sources or an additional project will be pursued to conduct more comprehensive studies on the bio-effects of and perform a field trial of the prototypes.

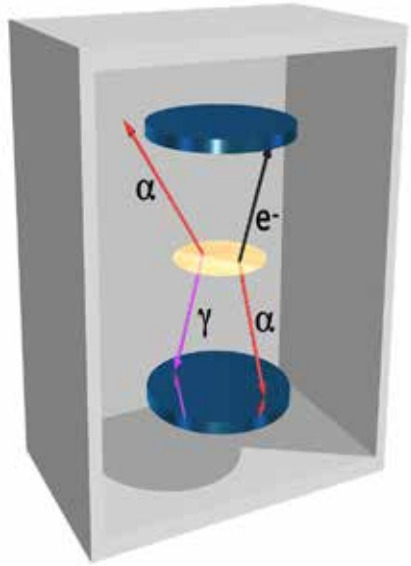
PN15082/2757

Alpha Coincidence Techniques for Actinide Assay

Glenn A. Warren

The effectiveness of conventional measurement techniques for environmental monitoring is limited by background and other interferences. This project will develop and demonstrate a new concept in radiation detection that disentangles these interferences and reduce background to improve our ability dramatically to assay environmental samples.

Examples abound of how actinides have been used in environmentally related studies. By measuring the ratio of ^{240}Pu to ^{239}Pu for example, one can determine whether a source is consistent with local or global fallout. Transuranics are strongly associated with particulates in water so that they can be used to study scavenging, the removal from water by attaching to particulates. The activity of plutonium as a function of depth beneath the sea floor surface has been used to measure bioturbatory processes that mix the surface into the rest of the sea floor. Likewise, other elements have been used to date fossil corals or carbonate rocks and study seasonal variations in river and sediment flow. Sample preparation requires time, resources, and people to complete. While the effort required to complete a few sample preparations may not be particularly arduous, there are many studies in which thousands of samples are collected, as some environmental science questions require easily scalable measurement techniques. Thus, minimizing sample preparation is an important aspect of the overall environmental monitoring effort.



Conceptual drawing of coincidence detection system, in which coincident α's and electrons are measured in separate silicon-based detector.

Any alpha-decaying radioisotopes have significant interferences when using current alpha-spectroscopy capabilities. By measuring other signatures that are generated in coincidence with the alpha particle, one can increase the probability of removing interferences between different radioisotopes. A good example of an isotope that may benefit from this approach is ^{238}Pu, which is not typically measured with mass spectroscopy techniques because of interferences with much larger quantities of ^{238}U. It cannot, however, be measured using alpha-spectroscopy without chemical separations because of interferences with alphas from ^{241}Am. A system that is able to measure particles in coincidence with alphas from ^{238}Pu may eliminate the need for chemical separation and enable large-scale assaying of such samples. Thus, our project goal was to develop a radiometric assay system for alpha-decaying radioisotopes that focuses on coincidence signatures to increase the specificity of the system.

To assay actinides in environmental samples simultaneously and rapidly, we are developing a detector design capable of observing coincidences between conversion electrons and alpha particles to assay on complex samples. Our objective was to demonstrate a new detection modality that could significantly enhance radiometric assay capabilities for a variety of applications requiring assay of actinides in complex samples. This new approach has had the potential to reduce assay time significantly, provide new sample diagnostic capability, and be a fieldable technology.

In FY 2013, we completed an initial scoping study to understand various aspects of designing the detector system. These aspects include an improved understanding of the signatures, an understanding of the substrate impact that holds the sample, and a comparison of two basic detector approaches: dual-gas proportional counters and double silicon-based detectors. The most important finding was that in the absence of background, the approach should achieve reasonable measurement uncertainties in a few hours for relevant samples. In FY 2014, the project evaluated the feasibility of the measurement approach for realistic samples, addressing issues such as intense backgrounds and absorptive materials. In addition, the project gained significant experience with experimental techniques using different detectors. This experience enabled the development of a prototype measurement system. In FY 2015, the project concluded with the completion of construction of the prototype system, which included a 16-channel silicon detector with a Peltier cooler.

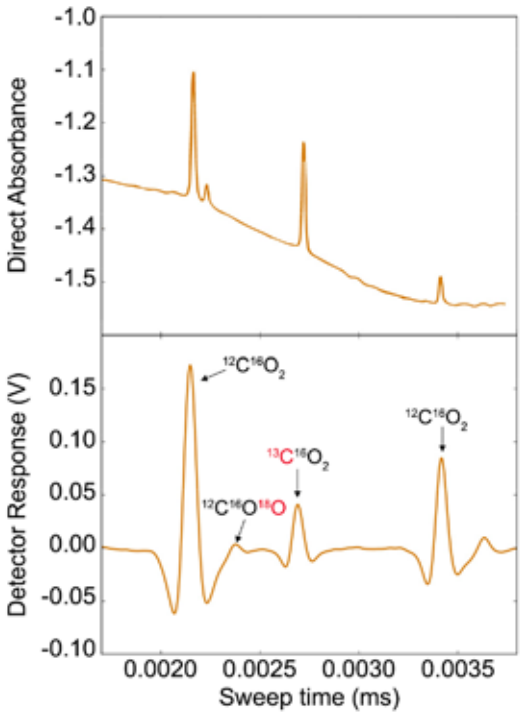
PN13019/2500

Combined Microscale ^{13}C and ^{18}O Measurements at Cutting-Edge Sensitivities and Spatial Resolution

James J. Moran

We are employing a platform to enable cutting-edge stable isotope measurement sensitivity for improving a range of new sample introduction techniques, thereby advancing research in diverse areas such as microbial nutrient cycling, forensics investigations, and ecological studies.

This project seeks to harness emerging advances in laser technologies to enable truly cutting edge measurement sensitivities for performing stable isotope analysis of carbon (^{13}C), oxygen (^{18}O), and sulfur (^{34}S and ^{33}S). The capillary absorption spectroscopy (CAS) system we are developing will provide orders of magnitude measurement sensitivity improvement over traditional analytical platforms, predominantly isotope ratio mass spectrometry (IRMS). Recent work with laser ablation sampling coupled to IRMS demonstrated spatial resolution of ~ 25µm when measuring ^{13}C over a solid surface. Ultimately, spatial resolution is controlled by the amount of sample required for analysis whereby higher measurement sensitivity would enable improved spatial resolution. While IRMS is traditionally the workhorse of light stable isotope analysis, it requires tens of nmoles of analyte for analysis. Combining laser ablation with a CAS-based measurement approach, this project seeks to enable spatially specific isotope measurement at scales not previously feasible and thereby enable a suite of potential stable isotope applications. Such a capability would provide new opportunities for exploring nutrient cycling in microbial communities, investigating small samples for forensic analysis, or studying small growth rings in animal tissues (e.g., fish otoliths or hairs).



This project developed software to collect raw absorbance data (top) and filter and quantify absorbance peaks (bottom) associated with specific isotopologuess. Importantly, this software is designed to facilitate a rapid data collection and average large numbers of scans to reduce the impact of background absorbance on measured isotope ratios. The process data shown was compiled from 6000 scans of the collected at 122 Hz.

For optimal usability and success, the instrument we are constructing must contain the following elements. First, a UV laser ablation

system must be present for selectively ablating a targeted region of a solid surface. A thermal unit designed to convert the ablated particulates into a gas (e.g., CO_2, CO, SO_2) is required, which is also amenable to interrogation by CAS. Specifically, a CAS unit must be available to receive samples, perform a measurement, and expel the sample. A software system for accurate, quick, and effective data processing is required to enable near real-time conversion of spectroscopic absorption patterns into isotope content data. Finally, integration of the above individual components is necessary to create one functional system. This project is focused on advancing our ability to perform these five key features while noting that once successful, additional sample introduction techniques (direct headspace analysis, gas chromatography, or others) could be applied with relatively minor effort. While many of the key system components can be supplied commercially, the CAS measurement platform and software to extract isotopic information from resulting absorption spectra is being pioneered at PNNL, and its development is the crucial technical accomplishment of this project.

Central to effective CAS is applying an infrared (IR) laser to a trapped sample gas and measuring the absorbance of vibrational transitions correlating to specific isotopologs. Advancing laser technology is expanding the wavenumber ranges that can be scanned via continuous wave IR laser spectroscopy, thereby enabling interrogation of superior sample transitions. We integrated laser availability with published absorption information (via the HITRAN database) to identify key laser/wavenumber ranges to optimize isotope measurement. In the

PN14023/2607

case of ^{33}S, we made primary absorption data to supplement the HITRAN database that did not previously include this isotope.

As with many new instrument development efforts, there was no pre-existing software to automate data integration and processing. The nature of optical interactions can create a number of noise/fringing features incompatible with optimal measurement sensitivity and accuracy. The software we developed contains a number of data processing steps that first help deconvolute a series of raw data points to reduce aberrant background/noise from the signal and secondly performs data integration to collect, process, and collate thousands of laser scans (generated on the order of seconds) and report a measured isotope value for the sample.

Optical feedback in the coupling of the laser to the capillary fiber or within the fiber itself can contribute to fringing or other background noise with negative impact on isotope measurement. We explored alternate designs to determine whether capillary geometry could be manipulated to reduce system feedback. Our results suggest that there are ways to significantly decrease optical feedback-induced fringing. Lowering the system's noise can lead to improved signal-to-noise ratios and ultimately improved measurement sensitivity.

IRMS has traditionally served as the primary instrumentation for stable isotope ratio measurements. Sensitivity limits and mass interference issues limit the application of IRMS to scientific questions that would otherwise benefit from stable isotope analysis. The CAS system being developed here offers vastly improved measurement sensitivity while also circumventing mass interference issues associated with IRMS. These features should enable stable isotope application to a wide variety of new applications.

Creating a Gas Phase Chemistry Workbench by Performing Manipulations in Efficient Ion Traps

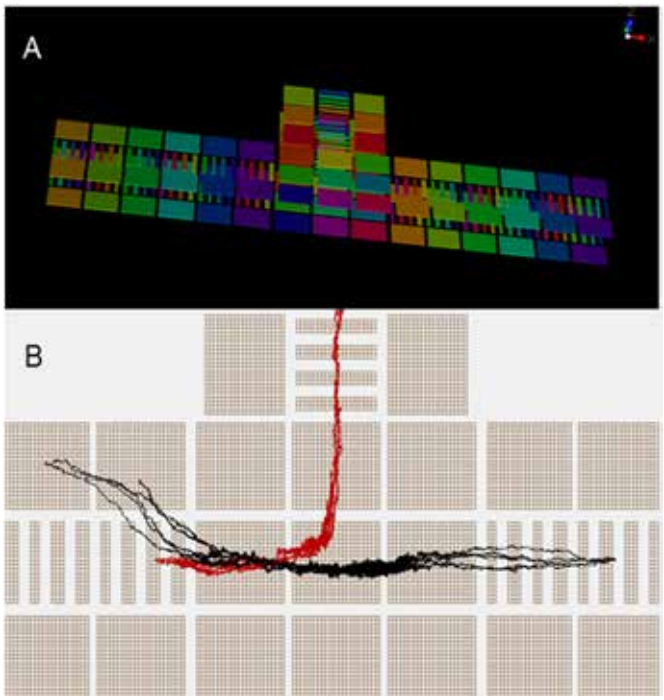
Erin S. Baker

This project seeks to demonstrate the feasibility of a gas phase chemistry workbench for performing lossless, highly efficient chemical reaction studies.

Our overall project goal is to develop new abilities for studying molecular level interactions based on extremely high speed and lossless gas phase ion manipulations. These manipulations will be conducted in readily fabricated and modularized PCB devices, which will create a gas phase chemistry workbench.

During FY 2014, we developed a gas phase chemistry workbench utilizing readily fabricated devices for the characterization of ion/molecule reactions. In this ion/molecule capability, a segmented PCB ion transfer device caused energetic collisions between ions of interest and target molecules, yielding dissociation reactions with high efficiency. For FY 2015, we worked on developing the ability to perform ion/ion reactions in the workbench. The first phase of development was to use the ion trajectory simulations to visualize ion/ion interactions in the workbench platform. The "A" figure shows the electrode layout for the ion/ion chemistry workbench. The design utilizes separate entrances for positively and negatively charged ions (left and right sides), a square central region where ions can interact, and an exit path above the reaction region (top) where product ions can enter the mass spectrometer for analysis.

Ion trajectory simulations as seen in the "B" figure predicted whether ions would overlap in the interaction region. The degree of ion trajectory overlap controls the extent of ion/ion reactions. Positive and negative ions losslessly traverse from each side to the central ion interaction region. The nine electrodes in the central region are each controlled by independent DC power supplies that allow ions of both polarities to be trapped and/or transmitted through the region. Specifically, the electrode voltages are applied to transmit negative ions through the interaction region while transmitting the positive ions through the swarm of negative ions and out of the interaction region for analysis. Simulations were conducted in another reaction mode where positively charged ions were losslessly trapped in the center of the reaction region. After accumulation of the positive ions, a swarm of negative ions entered the central reaction region. Positive and negative ions overlapped without the loss of any reactant ions (in this case, positive ions). The interaction time was controlled by maintaining the trapping DC potentials until release of the product ions was desired.



A. Layout of PCB ion/ion chemistry workbench; B. Simulated ion trajectories of positively (red) and negatively (black) charged ions in the interaction region.

PCBs were designed and printed based on the observation of the overlap of positive and negative ions in simulations. The electrode geometries were an exact match of the simulated electrodes. A vacuum chamber was designed and machined to interface negative and positive ion sources to the workbench using electrodynamic ion funnels. The exit of the ion interaction region was bolted to an existing mass spectrometer, where ions traversed through an ion funnel and two quadrupole ion guides into a mass spectrometer.

Once the ion/ion reaction workbench was assembled, positive ion transmission was optimized. After optimizing voltages in the interaction region, strong ion signals were measured with the mass spectrometer. Next, the ability of the new PCB device to conduct ion/molecule reactions was ascertained by dissociating ions via energetic collisions with background gas at pressures of > 4 torr. This assessment was accomplished by bringing ions closer to the board surfaces by tuning the DC potentials to cause interaction with strong local RF fields. Currently, we measured strong negative ion transmission into the workbench from the source, giving the ability to have ion/ion reactions, and are optimizing the device for highly efficient ion/ion reactions.

PN14074/2658

Development of an Ultra-Small Volume Detection and Sample Delivery System for Exploring Microscale Heterogeneity with NMR

Karl T. Mueller

We are developing methods and instrumentation that will ultimately integrate high-resolution NMR spectroscopy and MRI microscopy with lab-on-a-chip technology for studying sub-nanoliter samples.

Microscale heterogeneity plays a key role in determining the outcome of attempts to decrease pollution, optimize industrial production, or understand cellular-level processes. Because of the unique capability of nuclear magnetic resonance (NMR) to characterize biological and chemical systems in detail without significantly perturbing them, we seek to extend the reach of NMR spectroscopy to routine analysis of microscopic samples. To this end, we are developing methods and instrumentation that enable high-resolution NMR spectroscopy and magnetic resonance imaging (MRI) microscopy as a tool for studying microscale heterogeneity. The current generation of commercial small-volume NMR detectors requires sample volumes of 5–10 µL, and we intend to show that high-resolution NMR can be used for practical studies of volumes that are several orders of magnitude smaller, allowing for novel studies that address individual microsystems such as cells and aerosol particles.

Our first approach to preserve spectroscopic resolution with small-volume detectors involves two steps: first, develop a detector with near-optimal sensitivity for sub-nanoliter samples with high filling factor; and second, because the magnetic field homogeneity for this detector does not allow for high-resolution spectra, we used specialized pulse sequences to recover resolution.

In FY 2015, we completed all experiments related to these two steps and demonstrated that high-resolution ^{1}H and ^{13}C spectra can be obtained from (sub-)nanoliter samples on this detector. As of the end of FY 2015, a manuscript about this work is in preparation.

Currently, we are focusing on further design of the detector and the sample carrier to remove magnetic field inhomogeneity. Obtaining NMR spectra with sub-Hz resolution for sub-nanoliter samples without using customized pulse sequences will open the door to several new possibilities for small-volume NMR, including applications in single-cell metabolomics, microscale chemical reactions, and soft materials with multi-length scale inhomogeneity.

For FY 2016, our final step will be to design a narrow-bore probe with the detector that can fit into a gradient set, allowing demonstration of the technology in key applications in chemistry, materials science, and high throughput biological and environmental metabolomics studies.

PN14077/2661

Development of Coded Aperture Compressive Sensing Acquisition in Environment Transmission Electron Microscope

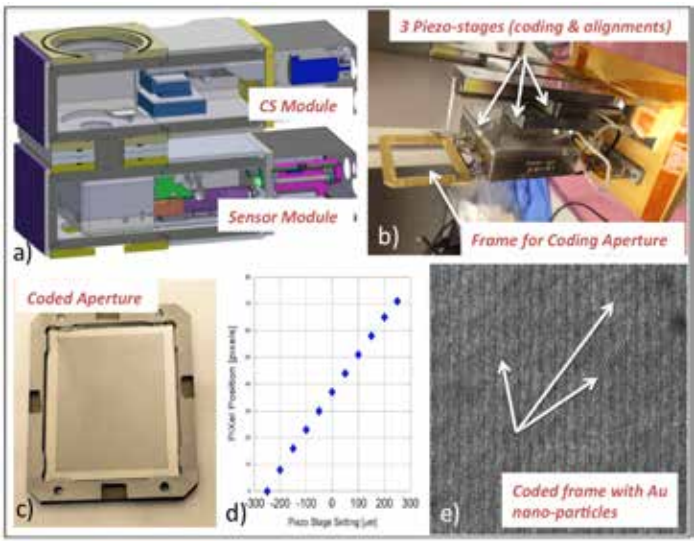
Libor Kovarik

We are developing temporal compressive sensing (CS) acquisition system to improve temporal resolution or correspondingly reduce electron dose by an order of magnitude comparable to conventional sensing.

Environmental transmission electron microscopy (ETEM) represents a powerful capability for resolving the structure of materials during exposure to gaseous environment. Modern aberration corrected environmental TEM instruments provide an angstrom level spatial resolution, which is required for the highest resolution of atomic level studies. In studying the transformation dynamics, however, the speed and sensitivity of the acquisition system represents the main limitation. To improve the temporal resolution of ETEM or alternatively reduce electron dose rate, we focused on developing temporal compressive sensing (CS), which is expected to improve temporal resolution or alternatively reduce the electron dose by an order of magnitude comparised with conventional sensing. To achieve the goal, we developed and built a prototype compressive sensing video acquisition system in collaboration with Direct Electron LP, one of the leading companies for manufacturing TEM acquisition systems. The design of the compressive sensing acquisition system was generally based on Duke University's optical bench compressive sensing setup that uses a coded aperture for temporal compression.

The CS camera was built modular: the upper portion incorporates the aperture and piezo-stage controls, and the lower module houses the actual acquisition device. An important effort of this project focused on developing the upper module. Namely, we designed a mechanism that allowed incorporation of piezo stages on the retractable plate to control the coded aperture. The aperture itself, which is the most critical components of the acquisition system, was designed and built as a part of this project. Compared with an optical setup, there are several unique factors for designing a coded aperture for high-energy electrons in TEM. We considered several possible designs and manufacturing processes and implemented one based on Apex glass etching. A custom aperture with 200 μm in thickness was manufactured by 3D Glass Solutions, Inc.

In addition to designing and building the camera hardware components, an important part of this project focused on designing and developing software controls for synchronized coding motion (piezo stage) during camera acquisition. We successfully implemented a scheme that allowed us to acquire coded images during forward and backward motion.



a) and b) Prototype of compressive sensing acquisition camera for ETEM. The prototype consists of upper module for coded aperture and piezo stage controls, plus a lower module for the sensor; c) The coded aperture in a support frame; d) A calibration curve for the piezo stage; and e) Image from a standard gold sample acquired using compressively sensing acquisition.

Next, the performance of the compressive sensing camera was tested on an ETEM. After resolving initial issues with charging at the aperture and Pt coatings, we showed that the as-built system is fully capable of acquisition under the compressive sensing acquisition scheme. Camera tests were performed on an Au grating standard sample and confirmed that acquisition with the coding aperture does not lead to any undesired image artifacts. However, the coded aperture as designed and manufactured does not meet the expected transmissive design performance, which prevented obtaining a successful video reconstruction. To move forward with compressive sensing on an ETEM, a redesign of the coded aperture to improve its tranmissive properties will be required.

As of the end of FY 2015, the work under this project has led to three scientific presentations and an article publication in the journal *Advanced Structural and Chemical Imaging*.

PN15047/2722

EUV Laser Ionization Mass Spectroscopy

Andrew M. Duffin

The objective of this project is to research the application of state-of-the-art extreme ultraviolet (EUV) lasers for rapid elemental analysis with particular focus on actinide materials.

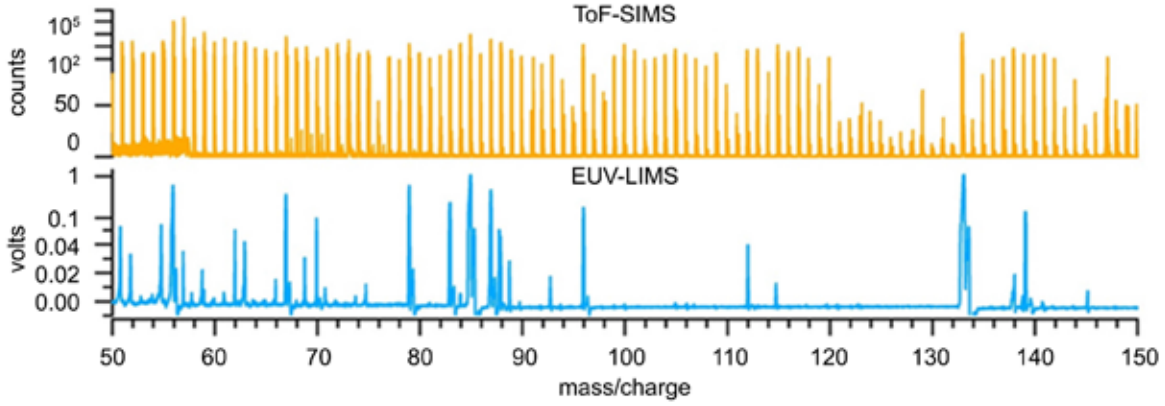
The recent development of reliable, tabletop EUV lasers has enabled performing laser ablation mass spectroscopy in a fundamentally different mode. While all laser ablation relies on multiple photons imparting sufficient energy to a solid surface to remove material, EUV laser light (46.9 nm or 26.4 eV) has at least 4 times more energy per photon compared to traditional laser ablation light (190–1080 nm or 6.5–1.1 eV). That is, EUV light is energetic enough to break even the strongest chemical bonds with a single photon whereas traditional ablation requires multiphoton excitation. In addition, EUV laser light can be focused down to approximately 100 nm spots, a roughly one to two orders of magnitude improvement over most commercial laser ablation systems. These features give the EUV technique great potential to dramatically improve the state-of-the-art in laser ablation coupled to mass spectroscopy.

Development of tabletop EUV lasers mainly comes from the Engineering Research Center for Extreme Ultraviolet Science and Technology at Colorado State University (CSU) in Fort Collins, CO. Researchers in this group have demonstrated the ability to ablate submicron craters and couple EUV ionized atoms into a mass spectrometer. In collaboration with CSU researchers, we are investigating the properties of EUV laser ablation/ionization along with the analytical capabilities of this new technique for elemental and actinide analysis.

This project received initial funding during the final month of FY 2014. This seed funding was used to meet with our collaborators at CSU to align expectations for the two research groups, develop a research plan, coordinate schedules for future experiments, and familiarize ourselves with EUV laser operation. As a result of this meeting, we identified a few key samples and pieces of equipment for purchase. We also agreed to a schedule for conducting experiments. This meeting positioned us well to begin meaningful work for FY 2015.

During FY 2015, we performed many of the experiments planned during the end of FY 2014. Specifically, we investigated the ability of EUV laser ionization mass spectroscopy (EUV-LIMS) to perform elemental analysis on a commonly used laser ablation standard NIST 610 glass, which was doped with 61 elements, each at approximately 500 µg/g. Consequently, it presents a complex mass spectrum with many possible molecular interferences. The main finding from the NIST 610 analysis was that EUV-LIMS produces a relatively interference free mass spectrum, wherein many elemental peaks are observed. Qualitatively, the detection limits for EUV-LIMS are tens to hundreds of parts per million, depending on the element. In addition, the ratio of elemental ions to molecular interferences can be increased with laser intensity.

Given similar probe volumes and the in-vacuum ionization, the most appropriate comparison technique for EUV-LIMS is time-of-flight secondary ion mass spectrometry (ToF-SIMS). The figure shows representative mass spectra from EUV-LIMS and ToF-SIMS and indicates that EUV excitation and ionization produce dramatically fewer molecular interferences compared with SIMS. Additional work is needed to improve the EUV-LIMS detection electronics, determine the sample utilization efficiency, and characterize the ionization process.



Mass spectrum of NIST 610 collected with ToF-SIMS (top plot) and EUV-LIMS (bottom plot).

PNL14091/2675

Free Form Millimeter-Wave Imaging

David M. Sheen

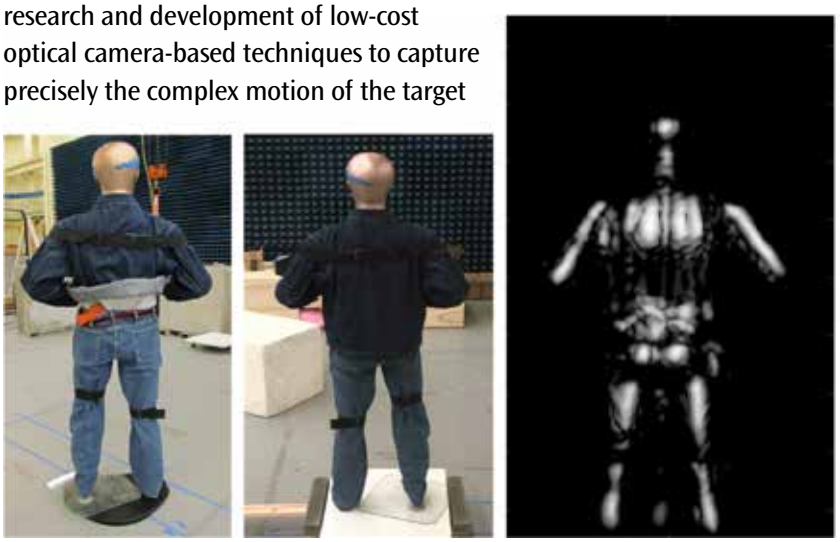
This project develops novel millimeter (mm)-wave imaging techniques that couple optical camera-based motion capture with linear arrays to enable flexible new 3D imaging modalities to offer enhanced performance.

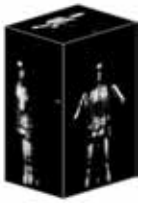
Micro and mm-waves can pass through many optically opaque materials, a property that is the fundamental basis for developing imaging systems for concealed weapon detection, in-wall imaging, ground penetrating radar, non-destructive evaluation of materials, and other security applications. A variety of novel imaging techniques have been developed at PNNL, all of which require precise scanning of a radar transceiver or transceiver array over uniformly sampled planar or cylindrical apertures. These techniques are seriously limited in their performance and range of applicability by the need for precise regular scanning over the aperture. Freeform imaging seeks to eliminate the requirement for standard aperture shapes and instead uses the motion of freely moving targets (or linear array) to sweep out a 2D irregular aperture. This process will allow for new applications such as scanning for weapons using a small mm-wave hand wand, scanning individuals as they walk freely past fixed linear arrays, and scanning walls using multiple overlapping manual scans.

Realizing the vision of freeform mm-wave imaging requires research and development of low-cost optical camera-based techniques to capture precisely the complex motion of the target or moving transceiver array and computational techniques to form focused 3D mm-wave images from data collected during the free-motion scanning. To this end, we focused in FY 2014 on developing freeform image techniques using synthesized and experimental data; acquiring and implementing a camera-based motion capture system; and experimenting with freeform imaging using the motion capture system coupled to a single channel transceiver for 2D imaging and a linear array for full 3D imaging. Prior to experimentation, custom numerical modeling was performed to assist in developing image reconstruction algorithms and to guide the experiments. The successful focusing in these simulations provided strong evidence that the algorithms were ready to test on experimental data.

For FY 2015, a large number of range by cross-range 2D and fully 3D imaging experiments were conducted of two fundamental types, moving target and moving transceiver. A single-channel transceiver was used to conduct 2D imaging experiments using both a fixed transceiver and freely moving target, and a fixed target and freely moving transceiver. A similar set of experiments was conducted using an available high resolution linear array. Results from all experiments show conclusively that diffraction limited imaging is possible for these freeform scanning configurations if accurate motion capture of the target and array is obtained.

Our work in FY 2015 also developed the optical motion capture technology and a new set of experiments using mannequins and human subjects to explore concealed weapon detection application demonstrations. The Microsoft Kinect system was evaluated as a possible motion capture technology. This system can track motion to accuracies the order of 10 mm. Additionally, a large number of imaging experiments were conducted using marker-based motion capture on mannequins and human subjects (refer to the figures). Future development of this technology is being pursued through external funding proposals.





Freeform 3D imaging result in which a mannequin carrying a concealed handgun was manually translated in front of a 2.4 m linear array to collect 3D mm-wave radar data. A back-view projection of the 3D focused image is shown, along with a small perspective showing the back, side, and top view projections.

PN14013/2597

Hybrid Microchip/Capillary Electrophoresis Platform for Rapid, Ultrasensitive Bioanalysis

Ryan T. Kelly

We are developing a rapid, ultrasensitive, quantitative chemical analysis platform based on capillary electrophoresis (CE) coupled with electrospray ionization (ESI)-mass spectrometry (MS) using a novel microfluidic sample injector.

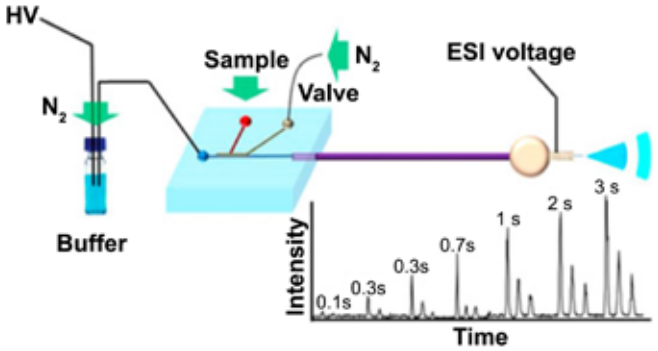
Rapid, quantitative and sensitive analyses are essential for advancing biological science and applications. We recently developed a novel injection mechanism for microchip CE, a powerful analytical separation technique widely used for proteomics, pharmaceutical, and biotechnology applications, that enables rapid, reproducible injections with no quantitative bias and allows variable sample volume compared with conventional electrokinetic injection. A pneumatic microvalve separates an analyte introduction channel from a separation channel at an intersection. The analyte introduction channel was pressurized such that when briefly opened, a small and volume-controllable sample plug is introduced to the separation channel. The high voltage was continuously applied across the separation channel, and analytes were rapidly separated. Polydimethylsiloxane (PDMS) was used as substrate material because its elastomeric properties were necessary for pneumatic valving. Unfortunately, PDMS has some undesirable surface properties (propensity to adsorb and absorb biomolecules, unstable surface charge) that limit separation efficiency. Also, difficulty in interfacing microchip electrophoresis with MS limited the proof-of-concept demonstration to fluorescence detection.

In this work, we are leveraging the numerous advantages of the microfluidic injector but performing the electrophoretic separations within fused silica capillaries to achieve high resolution separations. The platform will have significant advantages over either fully capillary or fully microfluidic systems. Also, the platform creates new analytical possibilities, including the facile coupling of liquid chromatography with CE-MS for ultrahigh peak capacity multidimensional analyses; as such, our work is expected to spur significant additional opportunities for development and application.

During FY 2015, we achieved our aim of developing a robust platform having microvalve-based microfluidic sample injection for CE separation within fused silica capillaries. In addition, we succeeded in implementing MS detection. A zero-dead volume interface was developed between the microchip and capillary by patterning a capillary insertion channel into the microchip. The geometry of the insertion channel was such that the capillary lumen aligned accurately to the microchannel terminus. To avoid leaks at the microchip-capillary interface, PDMS could be cured around the inserted capillary. Alternatively, the capillary insertion channel on the microchip could be undersized, requiring the PDMS to be stretched around the capillary, which also effectively eliminated leaking and dead volume at the interface.

We also greatly extended platform functionality by demonstrating that analyte preconcentration can be performed at the location of the closed microvalve. The closed microvalve, created by multilayer soft lithography, serves as a nanochannel preconcentrator under an applied electric potential, enabling current to pass through while preventing bulk flow. Once analytes are concentrated, the valve is briefly opened and the stacked sample is pressure injected into the separation channel for electrophoretic separation. Fluorescently labeled peptides were enriched by a factor of approximately 450 in 230 s. This method enables both rapid analyte concentration and controlled injection volume for high sensitivity, high resolution capillary electrophoresis.

For detection, a sheathless CE-MS electrospray interface was adapted from previous work. The interface was chemically etched to impart some porosity to the electrospray source, providing electrical conductivity through the capillary wall while preventing bulk flow. Combined with the absence of electroosmotic flow in the coated fused silica capillaries, the sheathless interface necessitated a pressure driven flow through the separation capillary to provide flow for ESI-MS. This worked well, but the process degraded separation efficiency somewhat. To overcome this limitation, we subsequently implemented an electrokinetically driven sheath flow interface that provided both high sensitivity as well as improved separation efficiency. We now routinely achieve >50,000 theoretical plates for our <10 min analyses.



Schematic of hybrid microchip-capillary CE platform

PN14058/2642

Low Background Light Sensitive Photo-Diode Array for Scintillator Readout

Michael E. Wright

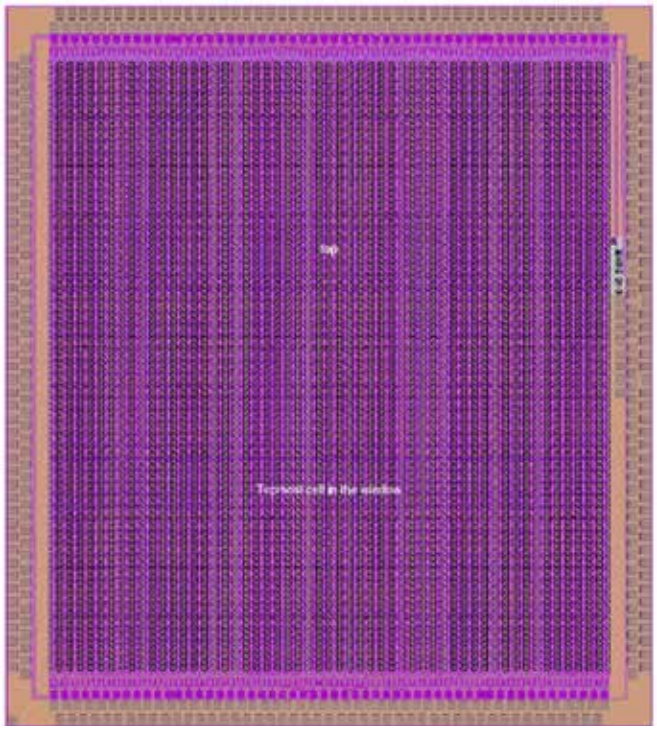
We have created a new ultra-high rate imager that is anticipated to revolutionize high speed detectors and cameras.

A broad gap in capability exists in imagers. Available commercial pixelated imagers are inadequate to the task of measuring the temporal structure of individual micro-scale scintillation, fluorescence, and luminescence light pulses. Measuring the temporal structure of these light pulses in real time allows for the identification of the nuclear and chemical conditions present in a sample and may enable a quantum leap in computer data storage that cross-cuts electronics from smart phones to exascale supercomputers, which is an extremely impactful area of human technical endeavors. However, specific continued advancement in these technical subjects is critical to maintaining state-of-the-art capabilities and driving successful commercialization.

Conventional imagers consist of pixel elements that form an image by reporting only the total light signal accumulated while the shutter was open. To create video, the imager accumulates images at the frame rate of 60 frames per second, for example. To make a slow-motion camera, the frame rate is increased to deliver many more images per second. To scale the imager specifically to the higher frame rates necessary to capture faster events, gigantic volumes of information must be transferred. Current imagers are not capable of this activity, cannot be made to run at the frame rate goals of this project, and are far too slow for the targeted fast process imaging.

The scientific goal of our project is to invent an imager integrated circuit (IC) with advanced capabilities to record light energy vs. time on the nanosecond time scale of single nuclear decay detections, enabling ultra-high frame rate cameras, ultra-slow motion electron microscope videos, single laser-driven fluorescence pulses, and optically stimulated luminescence (OSL) events in atomic-scale F-trap sites in optically stimulated luminescent materials. A secondary goal would be to create a sustainable new application-specific IC (ASIC) design capability at PNNL.

For the first 2 years of this project, we invested our efforts in establishing a new integrated circuit computer-aided design flow, a new imager architecture, and a number of new circuit inventions. Specifically, we created a new pixel element that functions in new ways. To accomplish our goal, we first replaced the accumulating pixel with a smart pixel that functions as a sampling oscilloscope, shrinking the volume of thousands of lab-bench-sized measurement instruments into a tiny IC. Second, we replaced the bottleneck of row or column pixel readout with a massively parallel readout scheme. We also created pixels with ultra-high time resolution but without the burden of a global clock network, where the pixels keep track of the short scale fine-grained time on their own. Each pixel stores a number of very fast events, rather than one single accumulation. A set of ultra-fast images are made and stored internally in the IC, which can then be read out either much faster than before or as only small areas. Detecting single nuclear events can also be read out and examined.



A computer representation of the imager.

Upcoming tasks for FY 2016 include the manufacture, packaging, and testing of the new 1,300,000 transistor imager prototype. With this demonstration, efforts to commercialize the technology and inventions created within this project will commence.

PN14033/2617

Low Background Liquid Scinitillation Counter

John L. Orrell

This project is developing a unique low background liquid scintillation counter to maximize the PNNL shallow underground laboratory's cosmic ray shielding. The system will be sensitive to β and α emitting nuclides at concentration levels 10–100 times lower than available from commercially available instruments.

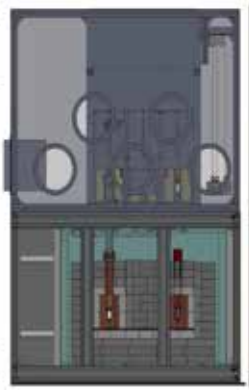
PNNL's shallow underground laboratory is intended for the measurement of low-concentration levels of radioactive isotopes in samples collected from the environment. Currently, development of a low-background liquid scintillation counter is underway to augment the laboratory's measurement capabilities. Liquid scintillation counting is especially useful for measuring charged particle (e.g., β, α) emitting isotopes with no (or very weak) γ-ray yields. The combination of high-efficiency detection of charged particle emission in a liquid scintillation cocktail coupled with the low-background environment of an appropriately-designed shield located in a clean underground laboratory provides the opportunity for increased-sensitivity measurements of a range of isotopes including tritium (^{3}H), strontium (^{89,90}Sr), or α-emitters in the naturally occurring uranium/thorium (U/Th) decay chains.

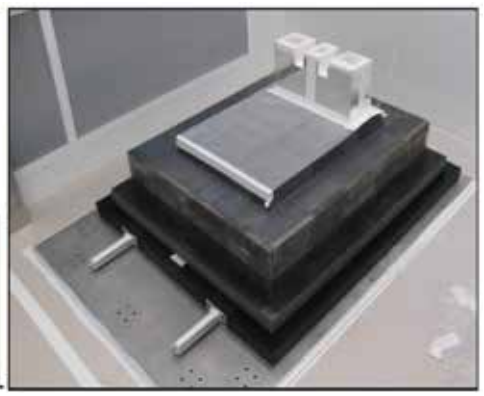
Our FY 2014 work covered three areas: low background shield design, novel light collection methods, and simulations for background estimates. Moving into FY 2015, our project had two distinct activities: final system design and procurement, fabrication, and testing of system components. The low background design follows a standard principle of nested active and passive shielding. From outermost to innermost, the shield is composed of a radon exclusion box, plastic scintillator panels for cosmic ray rejection, neutron absorbing 30% borated polyethylene, 8 inches of progressively lower ^{210}Pb concentration lead bricks to shield against external γ-rays, and a final inner 2-inch thick copper liner that also serves as the scintillation light collection guide. The novel light collection guide is designed as a hollow, highly reflective channel/guide milled within the inner copper liner. The reflective channels guide scintillation light from decays measured in the scintillation cocktail vial to photomultiplier tubes (PMTs) that are "around a corner" within the shielding so as to guard against trace radioactivity in the PMTs contributing to the background of the instrument.

The table image shows the radiation transport simulation results of anticipated background contribution rates. Commercial liquid scintillation counting systems typically report no better than 0.1 counts per minute of background. In contrast, the system under development may reach a background rate of 13.9 counts per day. The low background LSC design allows for several possible changes to current measurements employing liquid scintillation counting: enhanced sensitivity to trace radioactivity levels; reduction of initial sample size for fixed sensitivity requirement (e.g., regulatory requirements); reduced counting time for higher activity samples; and potentially reduced sample preparation chemistry.

Developments from this work are reported in the open literature, with papers submitted to or accepted by *Applied Optics, Applied Radiation and Isotopes*, and the *Journal of Radioanalytical and Nuclear Chemistry*. As of the end of FY 2015, the low background liquid scintillation counting system is under construction in the PNNL shallow underground laboratory. Work in FY 2016 will complete construction, make initial measurements validating the low background level of the LSC system, and demonstrate the utility of the low background LSC system for measurement of radioactive isotopes in the environment.

Background source (contributing isotopes)	Rate (cpd)	Fraction (%)
External γ-rays (U/Th/K)	2	14.4 %
Lead shield (^{210}Pb)	3.4	24.5 %
Copper shielding (U/Th/K/^{60}Co)	6.6	47.6 %
Light guide coating (U/Th/K)	0.008	<1 %
PMTs (U/Th/K/^{60}Co)	1.6	11.5 %
Vial plastic (U/Th/K)	0.15	1.1 %
Cross-talk (Presumed 2615 keV γ-ray)	0.03	<1 %
Neutrons	0.11	<1 %
Total estimated background rate	13.9	





A medium-fidelity Monte Carlo simulation of the radiation transport of a variety different background sources was employed to evaluate the liquid scintillation counter (LSC) system design. The table (left) shows the contributions for each of the backgrounds studied. The final design of the LSC system (center) is shown as an engineering model rendering. At the end of FY 2015, construction is underway in the PNNL shallow underground laboratory (right).

PN14001/2585

Mössbauer Spectral Imaging

Lucas E. Sweet

Actinide Mössbauer spectral imaging is a novel concept targeted at improving the limit of detection and chemical characterization of actinide-containing solids. This development is potentially a new tool in the field of radioactive material detection.

Mössbauer spectroscopy has been an underutilized chemical characterization technique for a couple of reasons. First, radiation sources to probe actinide nuclear resonances have been difficult to prepare and required significant radiological material handling infrastructure. Second, this has been a bulk solid analysis technique that required up to several days for a single spectrum to be collected on a sample. At these sample quantities and data collection times, other analytical techniques are more effective for chemical characterization.

Recent advances in iron (^{57}Fe) Mössbauer spectroscopy have drastically improved detection limits and data collection efficiency, including use of gamma detectors with high spatial resolution, gamma-ray focusing optics, and technologies for Mössbauer measurements using high flux synchrotron light sources. Our focus is to apply these advances in iron to actinide Mössbauer spectroscopy. These developments are intended to produce a novel ultra-sensitive characterization technique for actinide-containing solids that can have applications in nuclear safeguards and non-proliferation.

In FY 2013, we evaluated options and chose our detector, which was integrated into the spectrometer. We confirmed that the new configuration would allow for the high efficiency detection of the correct gamma-ray lines for performing our targeted actinide isotope Mössbauer measurements. The majority of our FY 2014 efforts focused on instrument design and the acquisition and fabrication of parts to make the design a reality. Several more custom parts were fabricated than originally anticipated because vendors were unable to produce parts that met our required specifications. We determined what kinds of gamma detectors were optimal for actinide Mössbauer measurements and the type of instrument geometries for optimal speed and sensitivity.

For FY 2015, many specialty parts were fabricated and acquired from vendors. The spectrometer was fully assembled in early July. Testing and adjustments were made using ^{57}Fe nuclear resonance to assure proper performance in a well-known system. After considerable adjustments and replacement of defective parts, we were able to demonstrate that the spectrometer is working properly and meets the specifications for performing actinide Mössbauer spectroscopy.

The resulting Mössbauer spectrometer developed in this project is versatile, safe, and cost effective relative to other instruments of its type. It can be configured to run in either a traditional transmission or backscattering mode. The unique design also allows for independent temperature control of the sample and source. In our instrument, the highly radioactive source can remain in the unit, shielded from workers while the sample is being changed out. Closed-cycle helium refrigerators were used in the design to reduce significantly the quantity of helium needed to run the instrument.

We designed, fabricated and tested a sample holder able to contain NpO_2 powder inside the holder during pressure swings from atmospheric pressure to high vacuum and temperature swings from room temperature down to −260°C. This sample holder did not leak after several temperature and pressure swings over the month long test measurements of NpO_2 purchased from the National Isotope Development program. We also learned that the ^{241}Am source purchased from Eckert and Ziegler is not suitable for Mössbauer spectroscopy. We were unable to collect a Mössbauer spectrum of the ^{237}Np sample because we did not have a suitable ^{241}Am source. One of the things that we learned from our visit with the operators of the actinide Mössbauer spectrometer in Germany was that actinide Mössbauer source fabrication is considered a lost art.

The actinide Mössbauer spectrometer equipped with two independent cryostats that can be adapted to a variety of different measurement geometries (e.g., transmission and backscatter modes)..

It is the recommendation of this team that investments be made in developing expertise and instrumentation for Mössbauer source fabrication capabilities.

PN13032/2513

Platform for Large-Scale Determination of Protein-Ligand Binding

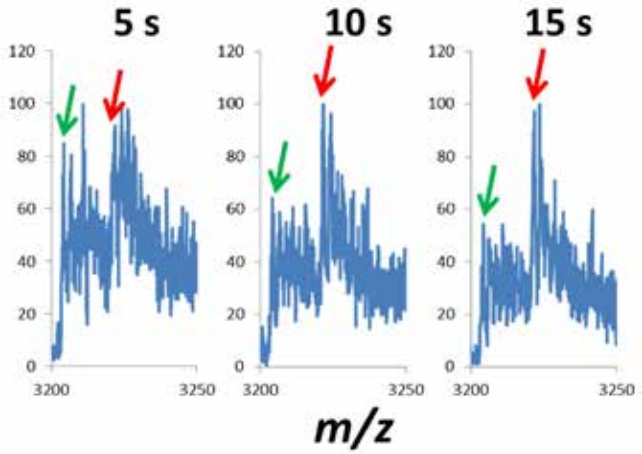
Ryan T. Kelly

We are developing a microfluidic platform and combining it with ion mobility spectrometry-mass spectrometry (IMS-MS) for the rapid determination of binding affinities and kinetic parameters associated with noncovalent protein-ligand interactions.

Noncovalent protein-ligand interactions play a major role in many biological processes including signal transduction, enzymatic catalysis and immune response. Determining the binding affinities and kinetics of those interactions is of great importance for applications ranging from biofuel development to drug screening. Our objective is to create and evaluate a new ultrasensitive, high-throughput, versatile protein/ligand interaction platform that will broadly advance fundamental and applied biological research. Measurements will be label-free, consume minimal amounts of sample and have substantially greater throughput than existing methodologies.

To accomplish the aims of this project, the microfluidic portion of the platform must have the ability to rapidly mix protein and ligand, incubate the mixed reagents for variable periods of time, and then deliver the reagents to an electrospray ionization (ESI) source for subsequent IMS-MS analysis at flow rates that are compatible with highly sensitive nano-ESI. The IMS-MS portion of the platform must have sufficient speed and sensitivity to obtain rapid measurements of free and bound protein with minimal signal averaging to preserve temporal resolution. The IMS-MS platform must also be sufficiently gentle to preserve the weak, noncovalent interactions of the protein/ligand complex such that the gas-phase IMS-MS measurements are representative of solution-phase binding. Beyond protein/ligand binding kinetics, the flexible platform more broadly enables generic time-resolved solution-based reaction monitoring by IMS-MS and MS alone that was not previously possible. Developments have now made it possible to follow the reactions that occur in the seconds-to-minutes range, and further ongoing developments will enable the monitoring window to be extended to both faster and slower reaction times.

The microfluidic portion of the platform was substantially simplified from what we originally envisioned, as the original droplet-based microfluidic devices were extremely sensitive to surface adsorption and had other issues that impeded robust operation. Further, the two-phase systems were difficult to clean and reuse, so new devices had to be made for each experiment. The current microfluidic system is droplet-free and highly robust such that a single device can be used for weeks with consistently reliable performance. The new design contains inlets for both protein and ligand that are each controlled by pneumatic microvalves precisely aligned just prior to the microfluidic mixer. Following the mixer, a fused silica emitter is interfaced with the microfluidic device for ionization. Following incubation for a given time, the ligand valve is opened to elute the reacted mixture. Thus, subsequent time points are obtained, with each equaling the pass-through plus valve closure times. In-house built programmable software enables all time points to be acquired automatically. Using the current configuration, each stopped flow time point is eluted for the amount of time that it takes to pass from mixer to emitter and as such, a tradeoff exists between the time amount of signal averaging that can be performed and the shortest time point that can be measured. There are several modifications involving new channel designs and variable eluting pressures that can alleviate this tradeoff.



Time-resolved mass spectra that represent 5, 10, and 15 s following mixing of 10 μM human carbonic anhydrase I with 40 μM of the inhibitor benzenesulfonamide are shown in the attached figure. Green arrows point to unbound protein and red arrows point to protein bound to ligand. The ratio of intensities for bound to unbound protein increases from 1.1 to 1.6 to 1.8 during the 3 measurements.

PN14022/2606

To achieve accurate protein-ligand binding measurements by IMS-MS, the conditions in solution must be close to physiological; otherwise, protein denaturation or other alterations may occur such that the measured affinities and rates are not representative of natural conditions. As such, the use of organic co-solvents and acids, which enhance ESI sensitivity, cannot be used. Also, the MS settings for desolvation and ion transmission must be kept as gentle as possible to avoid dissociating fragile protein/ligand complexes in the gas phase. Given these constraints and the fact that proteins already exhibit relatively poor ionization sensitivity, it is not uncommon for a protein/ligand solution to produce a signal intensity ~10^5 times lower than a standard peptide of the same concentration. The process has been a challenge, but we have been able to achieve such measurements with just a few seconds of signal averaging from the high ion transmission afforded by PNNL-developed ion optics. The enhanced sensitivity compares very well with that of other groups.

Dissociation constants (KD) for human carbonic anhydrase I bound to ethoxzolamide, acetazolamide, and benzenesulfonamide were studied with the IMS-MS platform to understand if the gas phase KD values agreed with solution-phase KD values measured with isothermal titration calorimetry (ITC). The IMS-MS platform measured KD values of 12 nM (ethoxzolamide), 1.5 µM (acetazolamide) and 4 µM (benzensulfonamide), which were in very good agreement with published ITC solution KDs of 9 nM (ethoxzolamide), 1 µM (acetazolamide) and 4 µM (benzenesulfonamide), indicating that the gas phase reactions were representative of solution-phase binding. After this initial evaluation, we started to study reactions that did not have known solution dissociation constants because we felt confident our instrument was preserving solution interactions.

One of the first set of complexes that we studied was the ligand diflunisal bound to the wild type plasma protein transthyretin (TTR) and its Leu55Pro variant (L55P), the most amyloidogenic transthyretin variant. Diflunisal is a drug under evaluation for patient use, where it would be desirable to stabilize the tetrameric form of the protein, thus inhibiting the unfolding that precedes fibril formation. Without diflunisal, the TTR and L55P proteins existed almost solely as tetramers with compact and extended conformations. TTR existed more as the compact form, which indicated it was more stable than L55P. This observation confirmed that the single nucleotide change (T→C) that produced the Leu55Pro variation caused sufficient structural changes in the expressed protein to effect the structural stability of the tetramer. Upon addition of diflunisal to TTR and L55P, diflunisal readily bound to both with a KD of ~900 nM and readily filled the two binding pockets when it was in excess. The extended conformation vanished in the ligand-bound complexes, indicating the stabilizing effect of diflunisal on the tetramers and its promise in stabilizing TTr and L55P. This work was written up in January and just recently accepted for publication in the journal *Proteomics*.

To use our understanding of IMS-MS with native protein complexes, we are also working with the Mayo Clinic to evaluate protein aggregation in patients with and without amyloidosis. Mayo Clinic has a quick protocol that can extract the immunoglobin light chains from serum in 5 minutes. They have found that these light chains aggregate for patients with amyloidosis but not to the same extent for patients that do not have the condition. Initially, we analyzed two clinical samples on the IMS-MS platform: one for a patient with amyloidosis and one for a healthy control patient. We performed a 15 s IMS-MS analysis and were able to see the difference easily between the patients due to the detection of excessive protein aggregation in the amyloidosis sample. Currently, we are waiting to analyze another 20 clinical samples to see if our initial evaluation holds true in a larger sample size. This study illustrates the potential for IMS-MS native protein analyses in the clinic.

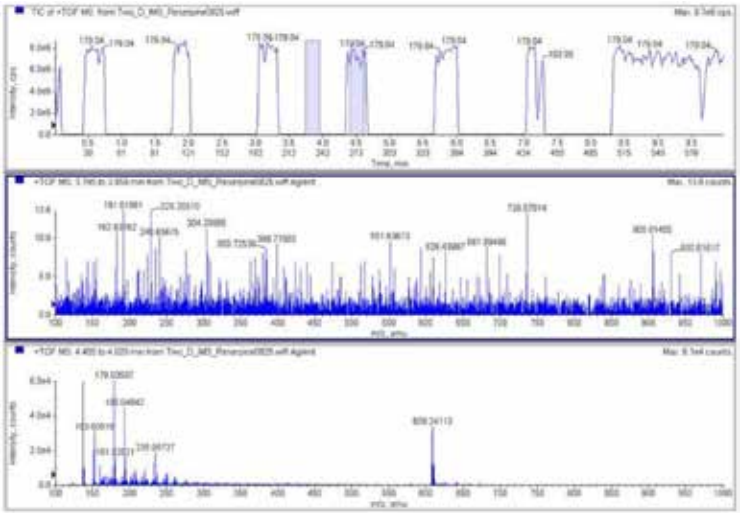
Single-Step 2-D Ion Mobility Separations Technology

Keqi Tang

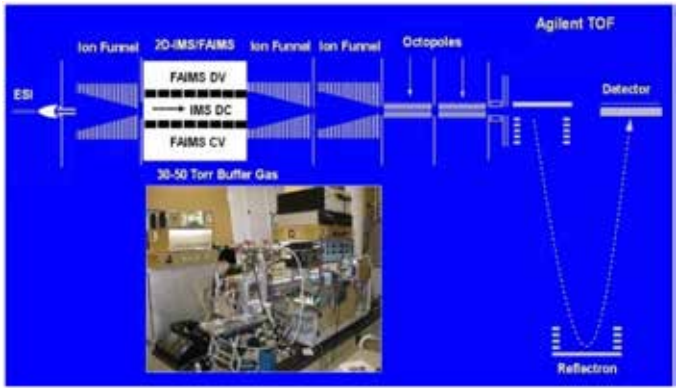
This project is developing a 2-D gas phase ion separation technology that combines ion mobility spectrometry (IMS) and field asymmetric waveform IMS (FAIMS) with high resolution and sensitivity.

Breakthroughs in chemistry and biology were historically enabled by new methods for molecular structure characterization. During the last decade, IMS coupled with mass spectrometry (MS) has emerged as the next powerful analytical and structural tool of broad utility and has included the rise of FAIMS from the dependence of ion mobility on electric field intensity. Strong orthogonality between FAIMS and linear IMS has prompted their coupling for 2-D gas phase ion separations of impressive combined resolving power (>1000). However, large ion losses at FAIMS/IMS and IMS/MS interfaces have made the sequential addition of these separation stages a major challenge preventing the practical utility of this extremely complex hybrid instrument.

The primary goal of this project is to develop a new instrumentation that allows single-step concurrent FAIMS and IMS separations by using a novel concept of field-driven FAIMS with electrodynamic ion funnel interfaces to achieve exceptional overall instrument sensitivity. Specifically, we are building the first longitudinally segmented FAIMS device and integrating it with an MS platform and demonstrate the performance of 2-D FAIMS/IMS separation for high throughput, high resolution, high sensitivity sample analysis.



Initial evaluation of 2-D IMS/FAIMS TOF MS using reserpine, segmented FAIMS CV scan 220–250 V DV at 600 Vp-p.



2-D IMS/FAIMS-TOF MS System

In FY 2015, our primary effort focused on building the first 2-D FAIMS/IMS device based on a well-known longitudinally-segmented FAIMS concept and implement the new device on a high performance time-of-flight (TOF)-MS using high efficiency electrodynamic ion funnel interfaces. The 2D-IMS/FAIMS system was installed in the first vacuum stage of the TOF-MS operating at 30–50 Torr pressure. To ensure high ion transmission efficiency, high pressure ion funnel interfaces were used at both the entrance and the exit of 2D-IMS/FAIMS system. The device was then configured to allow IMS and FAIMS separations to occur simultaneously in both horizontal and vertical directions.

Based on detailed theoretical analysis performed in FY 2014, the 2D-FAIMS/IMS device maintained a gap width between the two parallel segmented electrode assemblies that optimized FAIMS separation at the selected operating pressure range. Each segmented electrode assembly consisted of identically separated electrodes to allow uniform electric field in the horizontal direction for IMS separation. A FAIMS resolving power of 200 and an IMS resolving power of 30 were expected to be achieved, with an estimated combined FAIMS/IMS resolving power of 103 for the new device. With the capacitance matching between the new FAIMS/IMS device and the commercial FAIMS unit, we successfully developed a new asymmetric waveform power supply. After the successful implementation of the 2-D FAIMS/IMS device on a high performance TOF-MS, the new instrument platform was tested for initial performance under the segmented FAIMS operating mode. The ion signal was successfully acquired on the new instrument platform under the segmented FAIMS operating conditions using reserpine standard.

PN14079/2663

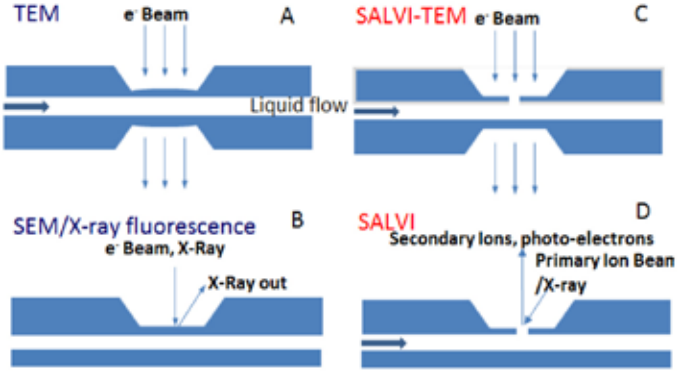
Universal Liquid TEM Microfluidic Cells Based on SALVI for Predicative Materials

Xiao-Ying Yu

We are developing a unique vacuum compatible microfluidic device that enabled direct imaging of liquid surfaces by multiple analytical platforms.

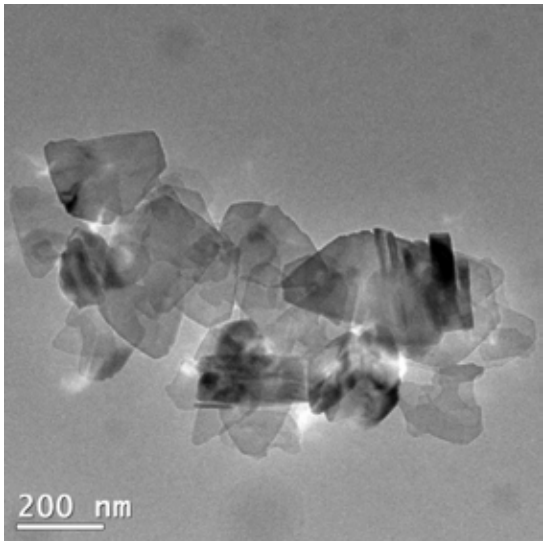
Transmission electron microscopy (TEM) is a widely used technique for material characterization with high spatial resolution at the nm level. The surging interest in the ability to study liquids using TEM has resulted in several companies offering specialized TEM holders for liquid imaging that are significantly more expensive than the standard holder. In addition, liquid TEM holders are incompatible with standard TEM specialized chips which, in liquid TEM studies, often have insufficient dimensions, limiting the sample types that can be analyzed. Although there has been design improvement to reduce sample bulging under vacuum, there remains a need for a universal liquid TEM device compatible with standard TEM holders with diverse applications and low cost.

We developed a unique vacuum compatible microfluidic device, System for Analysis at the Liquid Vacuum Interface (SALVI), that enables direct imaging of liquid surfaces by multiple analytical platforms. Extending SALVI to TEM enables analysis of the same sample with nm spatial resolution without altering the sample such as freezing or drying. This innovation will make liquid TEM analysis accessible to anyone with a TEM instrument for *in situ* dynamic material characterization without acquiring expensive sample holders and holder specific chips. We anticipate that our project will appeal not only to the microanalysis and microscopy community but also to anyone with research interests in material analysis involving liquid phases. As liquid TEM technology advances, it is anticipated that more people will begin to use this unique yet universal tool to study materials *in situ* in dynamic conditions. Moreover, it will allow more diverse studies in mesoscale imaging of material interfaces toward predicative material sciences for DOE.



Schematic illustrations of A) current liquid TEM cells; B) wet SEM cells; C) new SALVI-TEM; and D) existing SALVI.

SALVI contains a silicon nitride (SiN) membrane, an electron transparent material partially opened to vacuum via micrometer-sized apertures with liquid flowing beneath in a PDMS microchannel. Multiple micrometer-sized apertures can be opened to expose liquid surfaces to the probing beam (e.g., X-ray, electron, or primary ion beams) while liquid is withheld within the windowless holes by surface tension. This approach has been validated by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy (SEM). Many applications in biological systems (e.g., biofilms, mammalian cells) and material sciences have been studied. Unlike liquid TEM cells on the market, SALVI-TEM cells will have a small opening to reduce bulging based on the original SALVI concept. The size of the aperture will be optimized in this development.



AlOOH particles in deionized (DI) water sealed between two SiN membranes.

In FY 2015, we tested a variety of SiN membranes provided by Norcada to optimize the technique for assembling devices that has a thin layer of liquid enclosed in between. The SiN chips we experimented have different spacer thickness and vary in their shape, either round or square. The SiN window sizes are different too: rectangular are more favor-

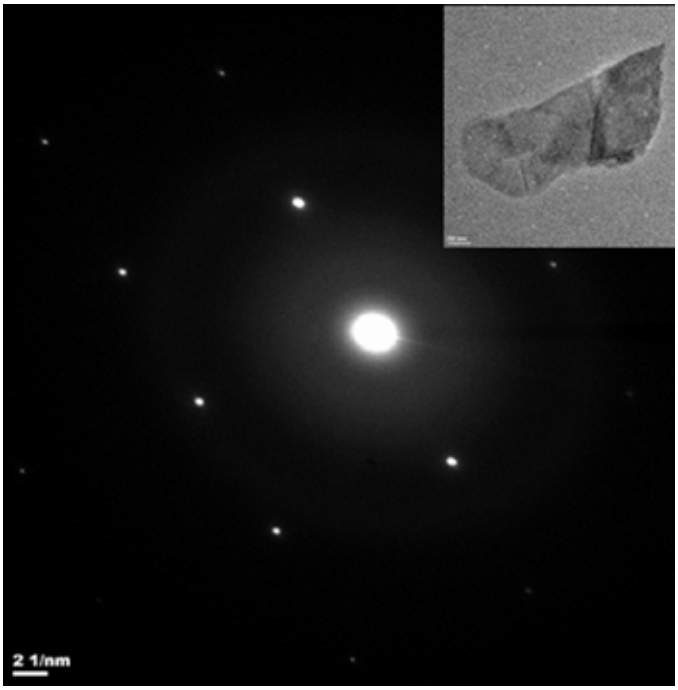
PN15087/2762

able to larger square windows. The SiN membranes are 50 nm thick and supported on a 100 μm thick Si frame. We determined that the square TEM chips with either 400 nm or 200 nm spacer are good choices for device assembly.

Several samples containing AlOOH (Boehmite) particles in DI water were used to illustrate that we can safely enclose liquids between two SiN membrane windows and sustain high vacuum in TEM. The particle plate-like morphology is clearly visible in the TEM image acquired under high vacuum conditions. Boehmite particles are known to stick to each other to form aggregates. These features agree with what we observed when the liquid sample was analyzed several days after assembling the device.

Using a higher magnification, the insert in the figure depicts a TEM image of a single AlOOH particle in DI water. More importantly, X-ray diffraction measurement was conducted to determine the crystal structure of the single particle in water. The distinct diffraction pattern shows that the crystal lattice of this material should be rhombic. This means that the AlOOH particle is not pure Boehmite, rather pseudo Boehmite. Pure Boehmite is known to be cubic, where pseudo Boehmite is reported to be rhombic. The latter finding is from recent TEM characterization of the dry Boehmite sample using high resolution TEM performed at PNNL.

These initial results show a great promise of our SALVI-TEM approach in its potential to elucidate nm-sized particle structure and morphology in the liquid environment using a standard TEM holder and TEM chips not specific to a particular holder. Our findings establish the following two milestones: we obtain the technical know-how concerning the assembly of stationary TEM devices; and we can use a standard TEM holder to study small particles in liquid in the high vacuum environment. They also establish important baselines for our next step of development.



An X-ray diffraction measurement of a single AlOOH particle in DI water. The insert shows the TEM image of the particle. The legend is 50 nm.

For FY 2016, we will study and optimize the aperture size in the TEM and develop a flowing cell that is adaptable to a standard TEM holder. As we learned how to assemble stationary devices that can sustain high vacuum in TEM, it is important that we optimize the aperture size to make SALVI suitable for TEM imaging. Because the stationary cell has only a very thin layer of water or liquid, the electron beam interaction on the liquid surface may quickly evaporate the liquid in vacuum, making it important that we flow the liquid to overcome beam damage and memory effect.

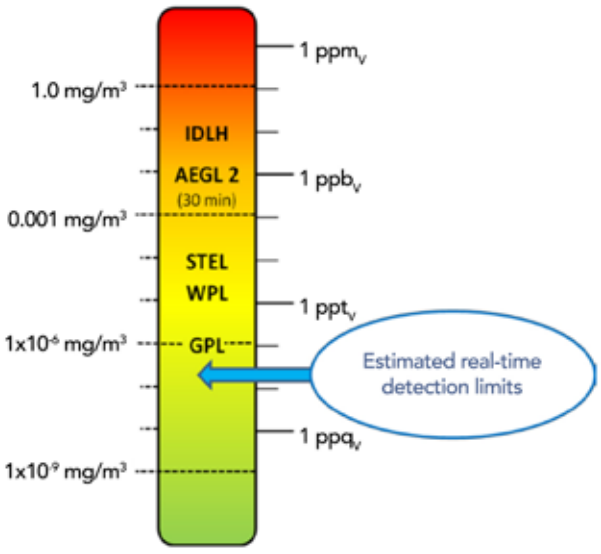
PN15087/2762

Vapor Detection of Illicit Substances in an Atmospheric Flow Tube Mass Spectrometer

Robert G. Ewing

Detection and interdiction of chemical weapon compounds and illicit drugs are important national security issues. This project is enabling real-time detection that is below occupational safety exposure levels and significantly lower than previous technologies.

The recent development of an atmospheric flow tube-mass spectrometer (AFT-MS) enabled the real-time vapor detection of some explosives at unprecedented levels, approaching a single part-per-quadrillion (ppq). These remarkable detection limits enable standoff or non-contact detection for a variety of scenarios, including cargo screening. In turn, this discovery led to the desire of determining what other substances, such as narcotics or chemical weapons, might be detectable at these levels. The challenge is that many of these compounds form positive ions, unlike explosives that form negative ions. Preliminary studies using AFT-MS have demonstrated complex positive ion spectra for background laboratory air. The primary scientific challenge associated with using the AFT-MS to detect positive ions of illicit substances is ionizing the target substances selectively in the presence of a variety of compounds in room air. The goal of this investigation is to identify and select appropriate ionization chemistries to reduce the interference of background chemicals while enabling the detection of illicit substances.



CDC recommended airborne exposure limits for nerve agent sarin

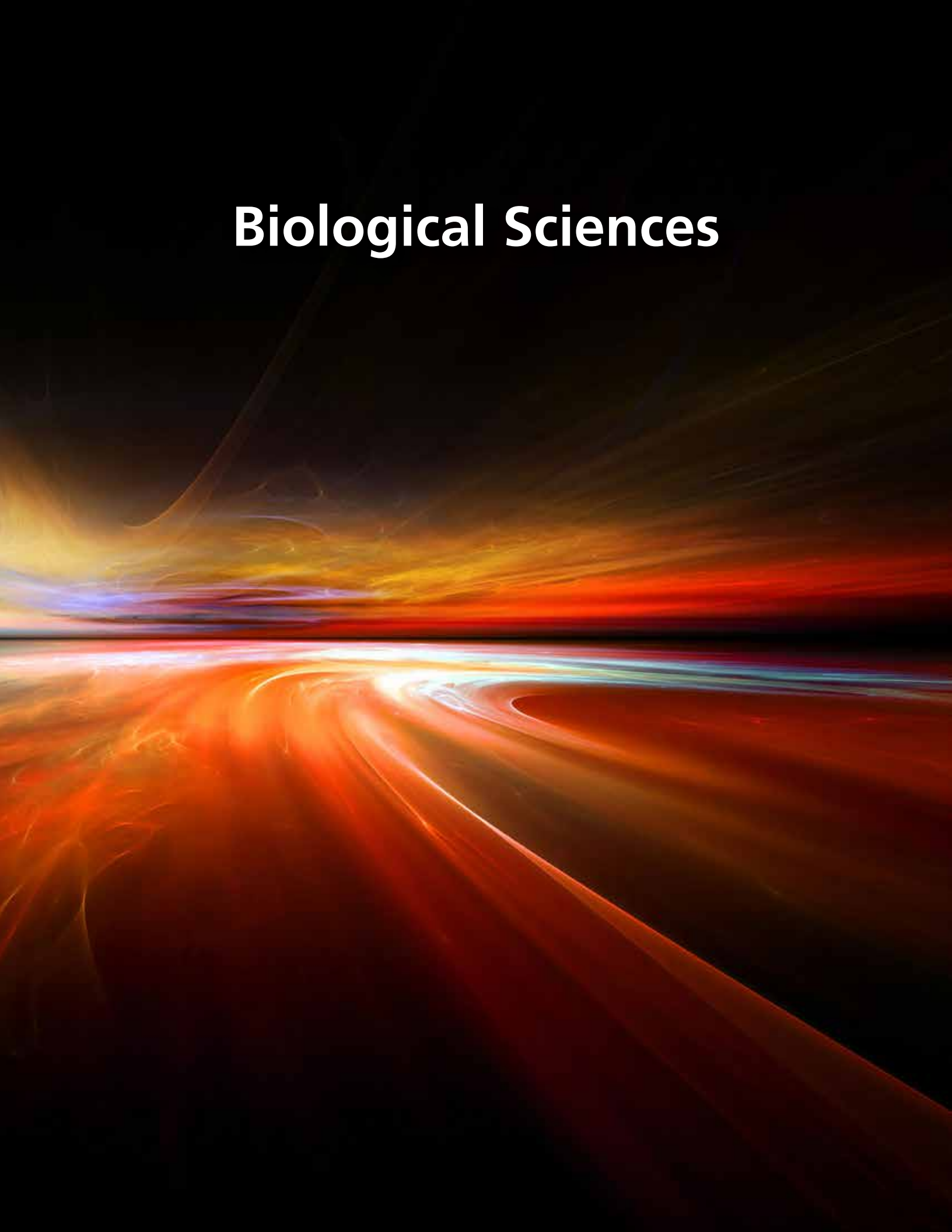
In FY 2014, two narcotics and two chemical weapon surrogates were evaluated with an AFT-MS to determine the substances' ability for ultra-trace vapor detection. It was determined that with the proper selective ionization chemistry, all four substances were detectable. For the narcotics, vapors from micro-gram quantities were detectable; for the chemical agent surrogates, vapor was detected from material permeating through the septa of a sealed 2 mL glass ampule. Preliminary data based on calculations of signal intensities suggest detection limits approaching single digit ppq. Further, vapor concentrations coming from the sealed vial with a dilution flow of ~7 L/min were estimated to be ~5 parts-per-trillion.

To varying degrees, all four substances responded differently to changes in the selective ion chemistry. In one instance, the selective ion chemistry produced a response 1600 times greater than that measured in room air. The selective ion chemistry in conjunction with the AFT-MS provided unprecedented detection limits for the compounds investigated. The system also provided unparalleled selectivity with the combination of selective ionization and mass spectrometry for positive identification with MS/MS for additional compound confirmation. With ppq detection levels in real-time without solute pre-concentration, this technology not only enables a revolutionary detection capabilities but it also provides a means to monitor analyte breakthrough at ultra-trace levels that will be useful in material development for personnel protection equipment such as gloves or protective suits.

In FY 2015, additional compounds were characterized, expanding the suite of chemicals that could be detected. Quantitation of both the ionization chemistry and analytes was performed. The optimal ionization chemistries were in the low parts-per trillion range. Under optimized conditions, the chemical weapon surrogates were detected at levels between 10 and 100 parts-per-quadrillion in real time. These levels were confirmed by 3 different methods: the first method used the relative peak intensities and a accepted equation, the second used a calibrated permeation tube and calculations were based on flow, and the third used known quantities of analyte that were injected and concentrations were calculated from flow rates. Values from all three methods agreed well, and the narcotics exhibited similar detection levels. Further, both substances were detectable in the presence of common solvents that were 6–8 orders of magnitude higher in concentration with little to no degradation in response. Thus, this method provides unprecedented sensitive and selective detection capabilities for these compounds.

PN14075/2659

Biological Sciences



Aperture

G. Christer Jansson

We are investigating environmental control of stomatal response in plant leaves with the objective of engineering bioenergy crops for improved water use efficiency.

Plants are sessile organisms, and their survival depends on efficient perception and response to the constantly changing environment. A major interface between plants and their surroundings is represented by stomatal pores formed by pairs of highly specialized guard cells. To maximize CO_2 uptake for photosynthesis and also minimize water loss, guard cells sense various signals and adjust the stomatal pore size accordingly. The manner in which the stomatal aperture is adjusted by the rapid movement of guard cells has fascinated plant biologists for decades. In addition, how abscisic acid (ABA) induces stomatal closure and how light induces the opening have been extensively studied. A plant hormone synthesized during drought to prevent water loss, ABA triggers a signaling network in guard cells that results in the loss of turgor and reduction of the stomatal aperture. The mechanisms for regulating stomatal closure and opening each involve distinct proteins kinases that regulate ion traffic across the plasma membrane.

The purpose of this project is to leverage EMSL capabilities for discovering how plant stomata is regulated by environmental factors in *Brachypodium distachyon* (Brachypodium, a genomic model for bioenergy grasses). Specifically, we aim to understand how parameters such as CO_2 levels, light, soil moisture, and temperature affect the aperture by regulatory mechanisms in the guard cells that make up the stomata. The project objectives during this partial year were two-fold: first, we wished to develop methods for imaging *B. stomata* by confocal and helium ion microscopy (HIM) specifically to enable characterization and capture in the living state. Second, we aimed to develop the technology for single-cell transcriptomics of Brachypodium guard cells.

HIM allows for sub-nanometer resolution of uncoated biological tissues. In combination with high pressure freezing, HIM allowed high contrast, high resolution imagining of stomata on the surface of Brachypodium leaf tissue in the living state. We demonstrated our capabilities to image intact leaves and epidermal strips sampled from drought resistant Brachypodium leaf tissue. Future studies will delve into plants exposed to drought and/or ambient and elevated CO_2 levels for different periods of time.

Single-cell analysis (SCA) will elucidate cellular functions within individual cells in response to changes in their environment that are not accessible from bulk measurements of heterogeneous populations. We demonstrated our abilities to isolate individual guard cells from whole plant tissue, a critical step prior to extraction of RNA and generation of a cDNA library from individual cells for RNA-seq.

Leaf tissues were cut from the central portion of the leaves and dissected according to published procedures. A shallow cut was made with a sharp razor blade horizontally across the leaf and a flap of leaf tissue lifted with a razor, leaving the lower epidermis intact. After being removed from the epidermis with forceps, leaf tissue immediately floated cuticle side up on an incubation buffer. Dissected leaf samples were imaged, with transmitted light and red images collected in two channels and overlayed. No staining was introduced prior to confocal imaging, and tissue samples were consistently wetted by incubation buffer during imaging to prevent drying of the sample.

Abaxial layer from a Brachypodium leaf blade.

High pressure freezing (HPF) of Brachypodium leaf tissue was performed, after which leaf samples were fixed by the 2-h fast freeze substitution method and endured multiple washes in two different solutions. Once all water was removed, the fixed leaf tissue was carefully transferred to the critical point dryer. The samples were purged with cold liquid CO_2 (~2°C) at elevated pressure and brought to supercritical pressure and temperature (42°C, 1200 psi) for incubation and equilibration. The pressure was slowly reduced while maintaining supercritical temperatures greater than 32°C. After the bleeding process, dried samples were transferred to HeIM holders with carbon tape and stored until imaged.

HIM was performed at 25 keV beam energy with a probe blanker ranging from 0.2–0.7 pA. In some instances, 2–7 nm of carbon was sputtered onto the leaf tissue to prevent charg-

PN15084/2759

ing effects. No post processing of the images were applied to the digital images. The image signal was acquired in a line-averaging mode with either 8 or 16 line integration to obtain the final image, where features were measured using the scale bar and line tool.

Leaf tissues isolated from the central portion of the leaves were dissected according to published procedures. Ethanol was fixed and placed onto a polyethylene naphthalate (PEN) membrane slide for laser capture dissection microscopy (LCDM) using a microeam. Guard cells were located, and identified cells were laser dissected from the surrounding leaf tissue and then collected. With one of our goals to preserve the leaf tissue in a living state that would reveal native cellular structures, we verified preservation of the stomata and plant cells by confocal fluorescence microscopy. High-pressure freezing methods were tested using the aluminum specimen carriers and different cryoprotectants. We then surveyed varying amounts of the fixative prior to critical point drying of the leaf tissue samples.

HIM revealed the surface architecture of the Brachypodium leaf tissue in fine detail. The mesophyll side of the guard cells was more clearly defined in the abaxial layer as opposed to the outer epidermal layer, where they appeared camouflaged by the surrounding tissues. High-pressure freezing clearly preserved the natural architecture of the leaf tissue surface and allowed long-term storage of different treatments and sample modalities. Ideally, imaging the native state of the leaf tissue would require additional adjustments to the fixation methods as well as eliminating the need for conductive coatings of the leaf tissue. However, our results clearly demonstrated that we can attain sub-micrometer resolution of the leaf tissue surface. Further experiments will utilize tissue-sectioning methods following treatment to reveal the native organization of organelles within the stomata and surrounding guard cells. Moreover, analysis of varying light, temperature, and calcium will capture the stoma in the varying open conformations in high resolution that will reveal further details of the Brachypodium and other plant stomata.

Having demonstrated the applicability of HIM in imaging Brachypodium stomata guard cells, we will aim in FY 2016 to dissect the structural and ultrastructural properties of the guard cells as they respond to different environmental fluctuations, including CO_2 levels, temperature, soil moisture, and light intensity and spectral composition. We will compare stomatal responses in Brachypodium plants with diverse degrees of drought tolerance. We will continue to develop the protocol for single-cell transcriptomics of guard cells with the goal of mapping regulatory processes underpinning stomatal response to environmental perturbations. HIM and single-cell transcriptomics will be complemented with metabolite profiling of guard cells during acclimation to perturbations. Of specific interest will be to monitor stomatal emissions and uptake of VOCs.

A specific focus of the project moving forward will be to investigate if and then how we can monitor protein phosphorylation *in vivo* as a means to identify kinases, phosphatases, and target proteins involved in stomatal responses to environmental cues such as shifts in CO_2 levels, temperature, and soil moisture. Achieving these efforts would put us in position to modify the phosphorylation status of stomata in crop plants as a means to improve water use efficiency.

Biological Threat Signatures for *Bacillus Anthracis*

Cynthia J. Bruckner-Lea

Distinguishing laboratory adapted from naturally occurring pathogens remains a challenge for the research and biodefense communities. This work will enable a more rapid identification of the source of disease outbreaks and a more effective response.

Previous work at PNNL has been focused on identifying and characterizing protein, carbohydrate, and other cellular signatures of pathogens grown in laboratory media. In addition, we have shown that the commonly used genomic tools for identification and characterization of pathogens are insufficient for providing information regarding whether an isolated pathogen has been cultured in a laboratory, which would be a likely prerequisite to its use as a bioweapon. This project was initiated to provide an in-depth investigation of both wild and laboratory strains of *Bacillus anthracis* using proteomics to understand the protein signatures that differentiate benign from potentially intentional infections. In addition to establishing protein signatures of *B. anthracis* domestication, we will establish for the first time whether these signatures are stable during *in vitro* infections of lung cells. This work will be a crucial achievement, as primary samples from infected patients may be the only source of samples for proteomic analysis. If *B. anthracis* is not available for this research, we will conduct similar studies using other pathogens of concern.

In January 2015, two of our team members traveled to Emerging Pathogens Institute at the University of Florida for our collaboration to establish a list of global wild and laboratory *B. anthracis* strains to be grown for proteomic analysis. We had a follow-up visit from them at PNNL in July 2015, during which time they brought grown and inactivated *B. anthracis* samples (80 total) for analysis and verified that the samples were sterile through extensive testing. Currently, additional samples are waiting for the lifting of a Centers for Disease Control and Prevention transport moratorium on *B. anthracis*. We anticipate that the samples will be shipped during FY 2016, after which time they will be processed and analyzed. We will use PNNL-developed lung tissue culture methods in Biosafety Level (BSL)2 space using attenuated *B. anthracis* strains to establish procedures for infection of lung tissue cultures, with virulent *B. anthracis* strains in BSL3 space for examining the stability of proteomic signatures following infection.

Another team member traveled to Ventura, CA in March 2015 for the Gordon Research Conference on Chemical and Biological Terrorism Defense and presented data about *Yersinia pestis* threat signatures, which were generated during a previous PNNL effort that led directly to this project. During the meeting, a partnering with Northwestern University was established that expands our project capabilities and includes a proteomic characterization of *Y. pestis* and *Y. pestis* infection and allows additional proteomic studies with *Y. pestis* while we are awaiting *B. anthracis* samples.

We were provided samples of lung fluid from *Y. pestis* infected and uninfected mice as well as *Y. pestis* samples for proteomics analysis (all samples were inactivated and noninfectious prior to sending to PNNL). This work investigated proteomic signatures of *Y. pestis* isolated from mouse lungs after infection and were processed without any laboratory culture steps. As expected, we observed significantly increased protein abundance in virulence determinants, but we also observed unexpected changes in central metabolism and stress response. The host response to *Y. pestis* infection was also investigated and will serve as a baseline for future studies using additional strains of *Y. pestis* from different evolutionary lineages. These data will comprise preliminary findings for upcoming external funding proposals in FY 2016 geared toward investigating the evolution of *Y. pestis* during its emergence as a potent human pathogen. On their own, these data also offer additional insight into protein expression in laboratory-adapted pathogen strains during infection, which will allow us to refine our main efforts investigating *B. anthracis*.

Finally, we invested a significant amount of time further analyzing existing unpublished data that supports project goals and drafting manuscripts. Specifically, we drafted two manuscripts describing the work to study long-term adaptation of *Y. pestis* to laboratory conditions; we modified a manuscript and added data to work that investigated the use of proteomic signatures of *Y. pestis* grown in different laboratory media for forensics; and we revisited work that examined the differences in proteomic signatures of *B. anthracis* spores produced in laboratory media versus soil. These four manuscripts will be submitted during FY 2016 and will contribute to our understanding of pathogen proteomics as they apply to attributing a source or sources to outbreaks of disease.

PN15061/2736

Chromatin Activity Precipitation (TIP)

Stephen R. Lindemann

We are developing a technology that would enable straightforward identification of regulatory mechanisms across microorganisms and eukaryotic cells to enhance the ability to predict organism behavior under changing environmental conditions and identify points at which microorganism functions may be controlled.

Chromatin activity precipitation (ChAP) is a novel approach to identify small molecule-bound regulatory proteins and the genes they regulate using PNNL-developed activity-based probes. The current state-of-the-art technology to determine regulator binding sites is chromatin immunoprecipitation (ChIP), which requires multiple variables: 1) *a priori* knowledge of which specific regulators are important; 2) cultivation of the organism in question; and 3) genetic tractability of the organism or generation of a specific antibody against the regulator. These conditions limit ChIP for use only in well-studied, tractable organisms and require a significant resource investment. In contrast, ChAP is an approach that is agnostic to the system in question, can identify novel regulators without *a priori* knowledge, and can be employed in environmental organisms without prior cultivation. Thus, ChAP has broad usefulness in studying metabolite regulation across organisms and in environmental samples and high commercialization potential.

The specific objective of this study is to develop a novel approach to elucidate transcription factors and their binding sites in cells based upon allosteric binding of regulators by small molecules. We are developing a suite of activity-based probes that mimic small molecular cofactors and irreversibly bind proteins *in vivo* to pull down complexes of probe-bound regulatory proteins selectively and target DNA or RNA as well as direct probe-RNA complexes.

Over the past year, we established a reporter system for the validation of vitamin B_{12}-mimic probes to the B_{12} *Escherichia coli* riboswitch, which is a regulatory motif within the messenger RNA that codes for the vitamin B_{12} salvage machinery known to bind vitamin B_{12}. When vitamin B_{12} is present, the cell senses via interaction of both the riboswitch and vitamin B_{12} that it does not need to import more, which thus stops translation of the salvage transporter. Initial experiments were aimed at identifying whether the vitamin B_{12} probe actually bound the riboswitch using a reporter construct, within which the riboswitch regulates the expression of a protein whose activity is easily measured (LacZ). Using the reporter assay that we constructed, we were confirmed that the vitamin B_{12} probe specifically binds the riboswitch, and that it does so with an affinity strongly similar to that of vitamin B_{12} itself. These data confirmed that our activity based probing strategy can target RNA regulatory elements directly without the indirect effects of a protein regulator.

Additionally under this project, we successfully expanded work performed in *E. coli* using a tryptophan-based probe performed under a companion project. We used a tryptophan-mimic probe to target tryptophan-mediated regulation in *E. coli*. We next expanded that approach to encompass tryptophan-based regulation in *Bacillus subtilis*, a phylogenetically-distinct organism. As *B. subtilis* regulates tryptophan biosynthesis using an RNA-regulatory protein complex, the *B. subtilis* reporter assay that we established allows us to target probe-protein-RNA interactions in addition to probe-protein-DNA and direct probe-RNA interactions. We also developed a click chemistry protocol that successfully identifies alkyne-labeled nucleic acids, a precursor for using our probe system, to identify nucleic acid-probe complexes. This advance brings us one step closer to an integrated approach to using metabolite-mimicking probes to identify regulatory complexes.

In FY 2016, we will develop the aforementioned integrated approach to isolation, enrichment, and analysis of probe complexes, demonstrating our platform as a useful tool and allowing for the commercialization of this work in ways that can be broadly employed to identify metabolite-based mechanisms of gene expression in both microbes and in tissues of multicellular organisms.

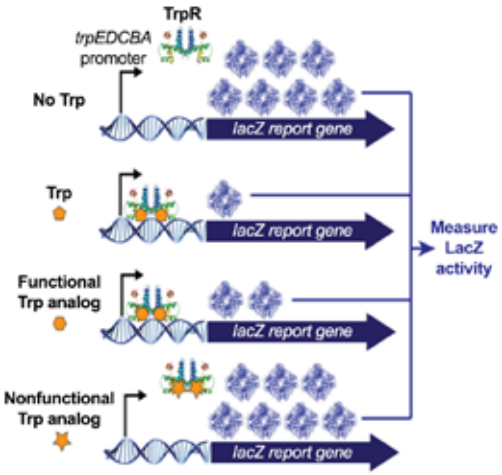
PN15083/2758

Cultivation-independent Untangling of Microbial Gene Regulation Networks

Stephen R. Lindemann

We designed an approach to identify the gene regulators in uncultivated microbes using molecular probes that mimic metabolites of interest.

Despite over a century of attempts, less than 1% of the world's microbes are currently thought to have been isolated and cultivated in the laboratory. Our inability to separate the remaining >99% stems largely from the fact that in nature, microbes are almost are almost never found on their own but rather exist as members of diverse microbial communities. As community members, they typically interact strongly with each other, exchanging resources as they cooperate and compete with one another. In contrast to macroorganisms, member interactions in microbial communities occur at the molecular scale and are difficult to decipher. The mechanisms by which a community's function changes between those conditions cannot be determined. Microbes are known to regulate the genes tightly they express in response to environmental cues. In many cases, detected changes in function may be due to a long series of compensatory changes, thus making it impossible to discern which of the responses observed by metatranscriptomics are reactions to environmental change and which are responses to the responses of other community members. Ultimately, a lack of a mechanistic understanding of gene regulation in microbial communities hampers our ability to predict how these communities will respond to perturbation.



A transcriptional reporter system used to screen activity-based probes for functionality. In this case, a successful probe mimicking a normal metabolite (tryptophan) will bind the tryptophan repressor as normal and reduce reporter activity, while a non-functional probe will have no effect.

In this project, we are generating a system to identify the regulators that respond to specific metabolites and the genes they regulate to be employed in uncultivated organisms regardless of microbial species. To identify regulator-gene pairs, we are employing probe molecules designed to mimic the metabolites of interest that are modified to allow us to induce irreversible binding to their regulatory protein and enrich probe-protein-DNA complexes from a mixed sample. The probe-bound proteins can then be identified using proteomics, while the genes regulated by the regulators can be determined using metagenomics.

To demonstrate the feasibility of our approach, we examined one of the best-studied cases of metabolite-mediated gene regulation, repression of the tryptophan (Trp) biosynthesis operon of *Escherichia coli*. In this system, the regulatory protein TrpR responds to the intracellular concentration of Trp by binding upstream of genes encoding Trp biosynthesis, preventing their expression. Because the targets of TrpR are known, this system permits us to determine the sensitivity and specificity of our approach. We initially designed and synthesized a probe molecule based upon Trp but could find no evidence that this first-generation probe was capable of either entering the bacterial cell or binding TrpR. Fortuitously, however, this spurred us to generate a bioassay by which a wide variety of Trp analogs could be examined for their ability to enter living cells, bind TrpR, and repress gene expression by binding DNA. This bioassay then allowed us to determine first, that our modifications to promote enrichment were not positioned at the appropriate location on the Trp molecule and second, that modification at different positions on the Trp molecule were well-tolerated by TrpR. These findings led to the development of second-generation probes which, unlike the first generation, have been shown to enter the cell and bind TrpR. Further, our assay system identified the ideal position for adding structures for probes (a diazirine ring for binding to the target protein and an alkyne handle to attach groups for fishing out the target protein-DNA complexes), enabling a third generation of probe design. Additionally, protocols for click chemistry-mediated identification of alkyne-tagged DNA were developed.

PN15010/2685

In FY 2016, we will employ third-generation Trp probes to enrich probe-TrpR complexes to determine whether they bind correctly to their DNA targets via genome sequencing and proteomics. Once the expected E. coli targets of the Trp probe have been identified successfully, we will apply the probe in low-diversity experimental communities for use in mixed-species communities, after which we will synthesize probes that mimic other metabolites of interest (e.g., sugars) to determine which proteins recognize these metabolites and what pathways they regulate.

Developing a Next Generation Biogeochemical Module for Earth System Models

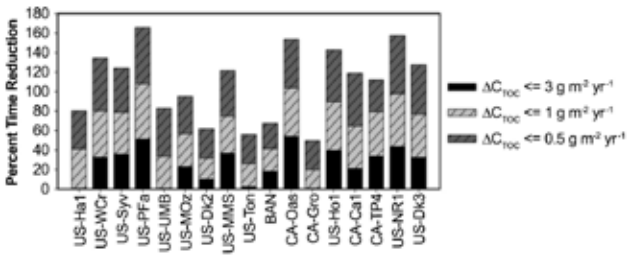
Yilin Fang

This research will bridge the gap between soil biogeochemical and earth system modeling research so that the representation of terrestrial ecosystem processes in land models can be used to improve the quality of climate model projections.

Biogeochemical processes regulate soil carbon dynamics and CO_2 flux to and from the atmosphere, influencing global climate changes. Integrating biogeochemical processes into earth system models (e.g., community land models [CLM]), however, faces three major challenges. First, extensive efforts are required to modify modeling structures and rewrite computer programs to incorporate biogeochemical processes with increasing complexity. These efforts must be repeated to integrate new knowledge being generated with time. Next, computational cost to spin-up CLM to steady state of coupled carbon–nitrogen processes is prohibitively expensive due to the long residence time of soil carbon. Finally, various mathematical representations of biogeochemical processes exist, some of which are too simplified to reflect fundamental mechanisms and others too complex for pragmatic application. A systematic evaluation of the different mathematical representations has not been performed in terms of their impact to climate prediction.

The objective of this research is to develop a generic biogeochemistry module to address the challenges mentioned above. This model will enable significant modeling research to be done in the future with reduced cost and minimize coding error. Additionally, we anticipate that the model will also facilitate the whole community to test different mechanistic process representations and data to gain new insight on what is most important in the system in response to climate change.

In FY 2014, we developed a new biogeochemical module that has a generic computational framework to readily incorporate mechanistic biogeochemical reactions into Earth system models for simulating carbon-climate feedbacks. A phosphorus cycle model was incorporated in CLM, the land component of the Community Earth System Model (CESM), using the new module.



During FY 2015, we developed an algorithm based on the new framework to directly estimate global soil organic carbon (SOC) using satellite-derived canopy leaf area index (LAI) and CLM, as soil carbon plays a key role in the carbon cycle that is important in global climate models. This is the first time that SOC is calculated using Moderate Resolution Imaging Spectroradiometer (MODIS)-derived LAI and without using the traditional long time spin-up of carbon-nitrogen (CN) models, often the bottleneck issue for global modeling and analysis. The results are comparable to those using the spin-up approach that can be a promising tool to estimate global SOC distribution efficiently and evaluate and compare different aspects simulated by different CN mechanisms in the model.

We developed a gradient projection approach to reduce the computation time of spin-up by 20–69% for point-scale simulations compared to one of the fastest approaches in the literature. During the study, we found instability of water table calculation in the hydrology model of CLM4 due to its local mass conservation error of water. The instability issue was resolved after we replaced the hydrology scheme in CLM4 with a PNNL-developed flow model STOMP for variably saturated porous media. We also replaced the microbially implicit first-order kinetic model for soil carbon decomposition in CLM with the Monod-type kinetic model that explicitly include microbial biomass and growth. We found discrepancies in the modeling results compared to the literature and are evaluating the causes. Our work has generated three manuscripts, two of which were published in *Geoscientific Model Development* and one in *JAMES: Journal of Advances in Modeling Earth Systems*.

We are working with another PNNL project, the Accelerated Climate Modeling for Energy (ACME), to incorporate the generic biogeochemical module into the river routing model MOSART to study biogeochemical processes in river systems. We are also participating in a multi-institutional site level model intercomparison study to evaluate the flow and biogeochemical models.

PN13007/2488

Dissection and Deciphering of the Soil Microbiome

Janet K. Jansson

Molecular-level information that provides insight into microbial processes performed by soil microorganisms should improve terrestrial carbon cycle models that predict climate change impact on soil carbon pools and greenhouse gas emissions.

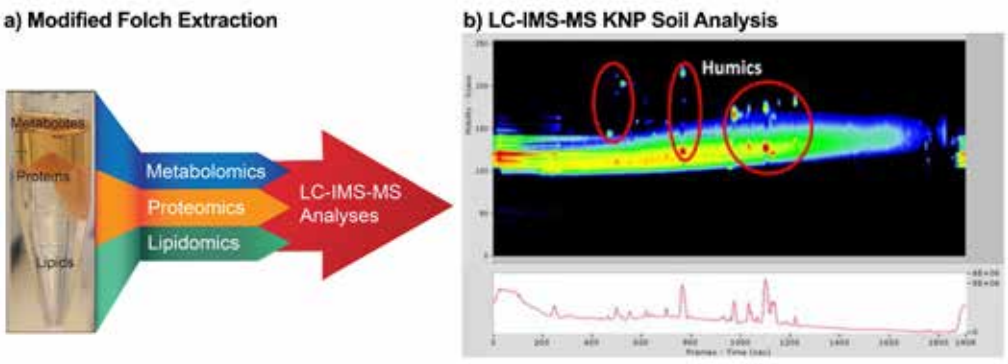
This project addressed key gaps in our knowledge about the composition and functional roles of the tens of thousands of microbial species in soil. Although these microorganisms carry out critical processes for life on earth, including cycling of nutrients and decomposition of organic matter, the majority (>90%) has never been cultivated, and their identities and functions are unknown. We developed and applied a suite of molecular tools and computational approaches to enable deciphering of the identities and key roles played by members of the soil microbiome. As a result, we improved our knowledge about the functioning of complex microbial communities, including their ability to process specific carbon substrates and react to nutrient additions. In addition, this work is highly relevant to the DOE Office of Biological and Environmental Research mission of understanding the terrestrial carbon cycle and climate feedbacks performed by soil microbes.

We developed and applied a combination of 'omics technologies (16S sequencing, metagenomics, metatranscriptomics, proteomics, lipidomics, and metabolomics) to Konza Native Prairie (KNP) soil in Kansas that is part of the Great Prairie of the United States, an ecosystem is of high interest to DOE because it represents soil that contains large amounts of carbon, and climate change has unknown consequences on the microbial communities in the soil and their ability to cycle the carbon contained in the soil. Specific project milestones are categorized and discussed below.

Soil metagenome assembly and analysis pipeline. To tackle the recognized difficulty in soil metagenome assembly, we applied a long read approach "Moleculo" combined with Illumina HiSeq sequencing for a hybrid assembly using the MetaHit assembly platform. This process enabled us to achieve the best soil metagenome assembly to date, with >6000 contigs greater than 10 Kb in size. By comparison, the best soil metagenome assembly for KNP at the Joint Genome Institute had 100 contigs >10 Kb, and the best published had only nine. In addition, with the application of new tools, we successfully annotated the metagenomes and binned several novel draft genomes representing previously undescribed members of the soil microbiome.

Soil glycine incubation experiment. Glycine is a model root exudate that is hypothesized specifically to stimulate growth of community members capable of rapid consumption of glycine as a substrate. We anticipated that addition of a substrate such as glycine would decrease microbial diversity and evenness, as taxa capable of metabolizing it would be enriched in relation to those that are not capable. We tested this hypothesis by incubating three Kansas prairie soils field replicates with and without glycine in triplicate for 48 hours, and characterized community level responses and the specific influence of glycine through 16S rRNA gene surveys and multi-omic analyses. All of the sequence data showed differences between the three soil locations, but not according to glycine addition, indicating the high variation between sampling locations in the field.

Macromolecule extraction protocols and analytical pipelines. During the incubation experiments, we developed and optimized methods for extraction of macromolecules from



a) The modified Folch extraction showing the metabolite (top), protein (middle), and lipid layers; b) LC-IMS-MS nested spectrum showing the humics (red circles) IMS separation from the peptides throughout LC gradient.

PN15054/2729

soil (DNA, RNA, protein, lipids and metabolites) and the pipelines for sample and data analysis. These established pipelines are now available for other samples that are generated, including soil and human/mammalian samples.

Activity-based probes successfully applied to soil. One of our aims was to dissect the soil microbiome into functionally relevant sub-communities prior to the application of multi-'omics technologies. To address this aim, we used a novel activity-based probe approach to identify the species and functionally active enzymes that may participate in metabolism of key substrates in soil. To establish the technology, we designed and successfully tested these probes targeted to glycoside hydrolases and monooxygenases.

As the result of this project, four manuscripts are currently in preparation (as of FY 2015 end) and will be submitted to journals during the next fiscal year.

Drugs of Abuse Retention and Degradation in Environmental Biofilms

Eric M. Winder

This project uses PNNL's expertise in biofilms and world-class instrumental analysis facilities as a means to investigate drugs of abuse retention, degradation and detection in biofilms.

Currently, the ability to detect drugs of abuse and other chemicals in non-traditional locations and throughout the environment is limited. Biofilms will capture and retain materials such as DNA and heavy metals from the surrounding environment. To be sure, biofilms are found in most environments, particularly at the interfaces of solid, liquid, and atmospheric environments and may range in appearance from the dry desert varnish found on rock surfaces in arid environments to the more familiar "slimes" including periphyton found in aquatic environments. The structure of a biofilm allows microorganisms to form a distinct microenvironment that is separate from yet interactive with the surrounding environment. A critical feature is the matrix of extracellular polymeric substances (EPS) secreted by cells that reside in the biofilm. The EPS is composed of a heterogeneous mixture of polysaccharides, lipids, nucleic acids, and proteins. Each component of the EPS plays a particular role in providing protection, sorption capabilities, nutrient/waste processing, and/or planktonic release of progeny cells.

This project aimed to show that biofilms derived from laboratory sink drains could capture/retain drugs of abuse (methamphetamine, cocaine, heroin, codeine, γ-hydroxybutyrate, and methylone) and signatures thereof from the aqueous environment. Subsequently, we investigated the ability to detect these materials by isolation from the biofilm and testing, over a time (7 days) post-simulated disposal (spiking) event. Of particular interest was the molecular sieve capability of an established biofilm that allows it to capture, sort, and sequester particular molecules from passing water, a sort of sticky trap (cf. flypaper) for passing cells, chemicals, biomolecules, and metals. This collection potential has several implications, including the extent to which biofilms may create and preserve a historical record of passing chemistry.

Initially, we aimed to increase the basic science knowledge for the fate of the studied chemicals in the environment while adding new sampling and analytical capability to the forensic toolkit used to investigate crime scenes and suspect facilities. To accomplish our goals, we established biofilms with drugs of abuse at varying concentrations to determine the limits of detection for each compound on our custom LC-Nanospray-ESI Orbitrap (LC-NS-ESI) and selected reaction monitoring tandem (LC-SRM)-MS systems. Solid phase extraction (SPE) methodology was tested, but direct infusion of the samples was used for this research to determine presence or absence of the spiked drugs in the biofilm material. The spectral data (peaks) obtained from blank media and biofilm samples were compiled for background subtraction from the final data set, allowing simplification of the complex samples for target and degradation product detection.

Using the LC-NS-ESI instrument, we showed a large reduction in the limit of detection for codeine and heroin compared to values in literature (limit of detection [LOD] ~5 ng/mL c.f. 377 and 960 ng/mL, respectively), while the LC-SRM showed signification LOD reduction (<0.02 ng/mL) for all drugs of abuse tested. Specifically, the LC-SRM is useful only when testing samples for specific known compounds; therefore, to test for unknown transformation/degradation products, we used the LC-NS-ESI instrument for spiked sample analysis.

Parallel samples were spiked at 50 µg/mL drug final concentrations (single drug target per sample). Samples were processed/analyzed at four time points (Day 0, 1, 3, and 7). The drugs γ-hydroxybutyrate and heroin were not identified in the biofilm sample fractions over the course of the 7-day test, as the molecular ion peak detected was too similar to a media component for peak-only identification, while the other drugs (methamphetamine, methylone, codeine, and cocaine) showed identifiable signals from the biofilm fraction over the 7-day period. The cocaine-spiked biofilm fraction mass spectra also showed peaks indicative of benzoylecgonine and ecgonine methyl ester (known metabolites) as these peaks were not seen in the spiked water samples, which indicates a transformation or degradation of cocaine by the microbes present in the samples. These metabolites were seen in the Day 3 and 7 samples but not the Day 0 or 1, lending a means to backdate the spiking event.

During FY 2015, we showed that biofilms can retain drugs of abuse, and that these drugs can be transformed or otherwise degraded by the microbes present. As of FY 2015 end, a manuscript has been prepared detailing these findings, and contacts and presentations have been made with the U.S. Department of Justice to suggest future research opportunities. Along with other biofilm work, this research was also presented at an international conference. The sampling and analysis performed in this project could ultimately transition into a forensic toolkit for use by officers and first responders to determine if drugs are or were at a given location.

PN14085/2669

Exploring and Engineering Phototrophic-Heterotrophic Partnerships

Hans C. Bernstein

This project is identifying controllable, cooperative ecological phenomena employed by phototrophically driven microbial communities for conceptualizing and engineering multispecies biocatalytic platforms. The target application for this work is energy capture and transfer from renewable resources, light, and CO_2.

Microbial consortia engineering has become an established scientific discipline populated by interdisciplinary biologists, engineers, and ecologists. The methodology is based on assembling microbial communities through enabling, encouraging, or enforcing interactions between distinct cell populations and their environment. Applications have the widely accepted potential to contribute technology toward key social benefits such as biofuel production, carbon sequestration, and environmental remediation. The soundness of the consortia concept for biotechnology applications is supported by observations in nature: naturally occurring ecosystems optimized by eons of evolution are almost ubiquitously organized as interacting mixed communities. Of these, photoautotrophic microbial consortia are of keen interest to chemical and biological engineers as promising catalytic systems capable of utilizing renewable resources light and CO_2.

The objective of this research is to dissect metabolically coupled interactions within naturally occurring biofilms from unique environments (i.e., high temperature and hypersaline) to discover ecological cooperation strategies to build engineered microbial consortia. The focus will be on identifying natural biological phenomena between photoautotrophic and heterotrophic microorganisms that can be controlled and harnessed. Our research differs from previously reported microbial community studies because it will advance technical understanding in the context of fundamental and applied science.

Phototrophic–heterotrophic communities were investigated in three separate experiments. The first study used data provided (partially) by external university collaborators and established that both photoautotrophic biofilm communities were capable of producing biofuel "precursors." We also established the spatially resolved kinetics of photosynthesis and respiration in these systems, which was published in the *Journal of Bioresource Technology*. The second biofilm community study employed a novel flow-cell bioreactor designed and built for this project to culture and maintain benthic, hypersaline microbial mats. Advanced oxygen microsensor methods were combined with the novel PNNL technology laser ablation isotope ratio mass spectrometry (LA-IRMS) to resolve spatially photosynthetic oxygen evolution, heterotrophic respiration, and carbon fixation. The LA-IRMS methodology has already been published in *Environmental Microbiology Reports*, and the results portion of this experiment are expected to be published during FY 2016.

A high temperature "hot-spring" community was cultured in an advanced turbidostat bioreactor and tested for its ability to overcome light and oxygen stress as a community. Preliminary results suggest that the artificial phototroph-heterotroph community preforms marginally better (in terms of measured specific growth rate) than the axenic, thermophilic cyanobacteria controls. The results from this portion of the project were presented at an international conference at the end of FY 2015.

The physiology of marine cyanobacteria as potential drivers of synthetic photoautotrophic-heterotrophic consortia was investigated in greater detail by studying axenic growth and photosynthetic performance, for which two studies were completed. The first evaluated the growth and photosynthetic performance of *Synechococcus* sp. strain PCC 7002 under mono- and dichromatic light regimes, which found distinctions in photoautotrophic functional capacity based on the spectral quality of incident light. These findings were published in *Frontiers in Microbiology*. A second similar study employed an advanced feedback-controlled turbidostat photobioreactor to investigate/compare the growth and photosynthetic performance of *Synechococcus* sp. strain PCC 7002 to its transcriptional response during variable incident light intensities and oxygen tensions; a manuscript is under review as of the end of FY 2015. During FY 2016, this platform will be expanded to include heterotrophic pairing and targeted metabolic engineering for control of interactions.

Additional studies that have been published as a result of this project include an article in the international journal *Life*, an article at the end of FY 2015 in *Scientific Reports*, and a chapter in the forthcoming book Biotechnology for *Biofuel Production and Optimization*.

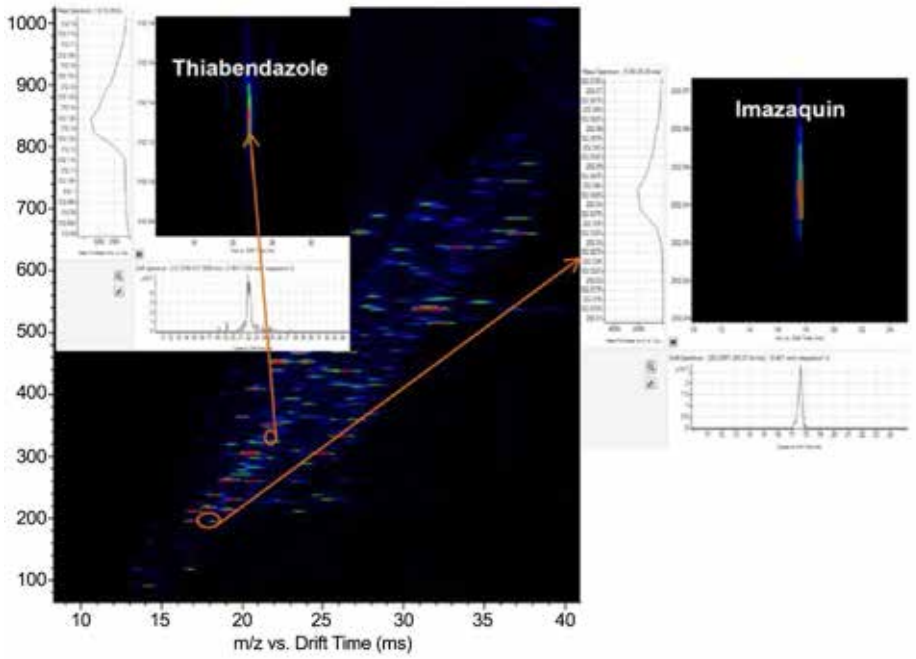
PN13101/2582

Global Forensic Chemical Exposure Assessment for the Environmental Exposome

Justin G. Teeguarden

Our goal is to perfect and apply technology that allows the measuring of thousands of chemicals that are important to public and environmental health in blood and other fluids used for biomonitoring. The technology will revolutionize the way chemical effects are studied, how safer energy technologies are developed, and how we predict and respond to global climate change.

Human and ecological health is widely recognized as the product of the genome and its environmental analogue, the exposome, the comprehensive history of exposures to natural and manmade agents within individuals and populations. One ambition of DOE's Human Genome Project was to use genomic information to predict the health of humans and the environment. However, without corresponding knowledge regarding human chemical exposure and its interaction with the genome, information from the Human Genome Project was not sufficient for making these predictions.



IMMS spectra of xenometabolites in human plasma (+ mode)

Advanced analytical instruments developed by PNNL offer the chance to provide this missing information by performing measurements that were previously not possible; i.e., quantifying hundreds to thousands of structurally diverse chemicals simultaneously within single samples of blood or other fluids used for biomonitoring of exposure. This project was initiated to perfect the application of PNNL's advanced instruments in making these measurements.

Specifically, our analytical approach used ion mobility spectrometry-mass spectrometry (IMS-MS). Developing a reference library of chemicals and their unique chemical signatures measured by IMS-MS, a central project goal, continued in FY 2015. These chemical signatures included the IMS drift times and accurate masses, which become the basis for the high throughput, accurate quantification of the chemicals. To date, we developed a reference library and signatures for nearly 500 chemicals (lipids and chemicals). To increase progress, we created a novel computational algorithm that automates library development. The software combines new approaches for identification of IMS-MS peaks, with novel concepts from field of computer visualization to provide rapid, highly accurate assembly of data and calculation of entries for the library. A manuscript describing this method has been drafted and will be submitted in FY 2016. We also continued to build on earlier findings that the IMS-MS platform provided extraordinary resolution and detected chemicals down to the parts per trillion range in solvents, ideal for analyzing tissue and fluids for environmental chemicals. We found that the IMS-MS technology can separate all of a subset of chemicals we tested from thousands of endogenous chemicals in blood (e.g., lipids, metabolites), paving the way for simultaneous analysis of endogenous and environmental chemicals.

With a goal of applying the IMS-MS technology to the analysis of human biomonitoring samples, novel approaches for the rapid analysis of blood and urine samples were the major focus of the FY 2015 effort. Our initial finding was that the large number of compounds in blood and urine reduced the

PN14030/2614

sensitivity of the approach. In collaboration with a major instrument developer, we pioneered integration of a new, ultra-fast separation system RapidFire with the IMS-MS instrument. After optimization of the method separately for blood and urine, we discovered that a systems combination dramatically improved detection limits of test compounds in blood and urine as well as increased the number of identifiable metabolites and xenometabolites. The RapidFire-IMS-MS system achieves detection limits in the part- to sub-part-per trillion level, while maintaining a sub-minute run time. An article about this work will be published in early FY 2016.

Significant progress was also made in developing advanced computational approaches for the prediction of the unique signature for chemicals without the need for experiments. Our approach was able to predict the unique chemical cross-sectional area of test chemicals with errors small enough to support identification of unknown structures when used in combination with additional meta data and a chemoinformatics platform. Advancing approach through development of a supporting chemoinformatics platform is a major focus of our efforts in FY 2016. In FY 2015, we also maintained partnerships with the U.S. FDA and the U.S. EPA which provided materials for advancing the methodology and opportunities for collaboration.

Three major goals will be the focus of FY 2016 research efforts. Publication of results in high impact journals is the highest priority effort for the first quarter, followed by submission of an NIEHS grant. The second major objective is to complete and publish the computational informatics approach for *in silico* prediction of collision cross section and the supporting algorithm for untargeted analysis of human samples. Finally, applying the system to analysis of human samples will complete this project.

Imaging and Monitoring the Initial Stages of Biofilm Formation

Raymond S. Addleman

The analytical capabilities developed in this project will enable unprecedented visualization, characterization, and understanding of the initial molecular and cellular processes involved in biofilm formation.

Systematic studies of initial stages of biofilm formation – the conditioning film and primary colonizers – are lacking in literature largely due to the complex nature of the problem and the absence of available tools for studying the process. We are leveraging advanced chemical imaging techniques developed at PNNL to improve the understanding of initial biofilm formation and subsequent surface biofouling. This interdisciplinary effort will provide better tools and a mechanistic understanding of the initial biofilm formation process on existing and novel material surfaces. Having new tools to study the processes that lead to biofilm formation will support the development of new, innovative, non-toxic means to combat fouling relevant to DOE missions in hydropower, efficient desalination, reduced environmental contamination, improved fuel efficiency for ship transport, bioremediation, and improved separations and catalysis as well as biomedical and other applications.

Key issues in our research include determining which new analytical methods are best suited to visualize and characterize the initial stages of biofilm formation. A critical challenge for the study of biofilms has been the lack of methods and instrumentation that can perform detailed measurements and monitoring of wetted surfaces. Another key challenge the development of methods that can measure young biofilms nondestructively enabling them be measured *in situ* and their development monitored over time. Finally, because biofoulings is an irregular process over surfaces, measurement methods preferably have the widest field of view possible while maintaining the best vertical resolution achievable (µ to nm).

We commenced this project by evaluating then-recent techniques and developing new analytical methods. The imaging and analytical techniques explored during this project has provided new tools for fundamental science studies as well as new methods for quantitative and qualitative biofilm assays for a variety of applications. These specific techniques in development include the following:

- MALDI-TOF has shown to be effective for biochemical characterization during biofilm formation
- Ultrasonic imaging have shown *in situ* monitoring of the growth of harder biofilms at the micron scale

The study of antifouling surfaces has resulted in the creation of a novel paintable superhydrophobic, ultralow surface energy, and self-healing surface that is nontoxic and has outstanding resistance to biofilm formation. Shown is the Chemical Imaging initiative acronym at PNNL painted in this water repellent coating, that clearly remains dry despite being surrounded by water.

- Sophisticated digital image analysis techniques has been shown to provide rapid accurate quantification of biofouling and are amendable to field measurements
- Low power UV light, similar to that found in LED flash lights, has shown the ability to perform *in situ* monitoring of biofilm growth.
- Optical interferometry has be shown to provide very sensitive nondestructive *in situ* monitoring of the growth of biofilms with a wide field of view (mm) and excellent vertical resolution (nm)
- We developed a new quantitative method for measuring total biofilm content on a surface and correlated it to standard methods as well as some of the selected newly developed techniques.

The above resulted in the creation of a novel paintable, superhydrophobic, ultralow surface energy, self-healing nontoxic surface that has outstanding resistance to biofilm formation as shown in the figure.

For FY 2015, we continued to explore the new methods to measure biofilms as they form and demonstrate them in new ways. This project focused on two high impact areas: marine biofouling and biomedical-related biofilm formation. The initial stages biofouling processes as a function of time and surface composition were quantitatively studied for the first time with these new methods. As of the end of FY 2015, we have three manuscripts under review and three others to be submitted during FY 2016. This project has also resulted in one patent application and two provisional patents as placeholders. Moving forward, we are exploring the process of having some of the next methods certified as new American Society for Testing and Materials international standards.

PN13067/2548

Impact of Environmental Stressors on 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.

The concepts of stability and resilience are key to promoting ecosystem sustainability in the face of significant climate change. The same fundamental principles are relevant to the maintenance of homeostasis (health) in complex organisms subjected to environmental perturbations. Our objective is to specifically target the flow of information from the genome to the functional level defined by proteins and metabolites, with emphases on the dynamic response to environmental perturbations and the communication mechanisms that allow complex systems – whether communities of microbes or organized tissues in multi-cellular organisms – to adapt to and mitigate perturbation. We will achieve these goals by applying systems biology approaches to quantitative data generated with unique PNNL instrumentation in MS, nuclear magnetic resonance, and imaging to understand the effects of environmental stressors on multi-cellular systems. We will select novel model systems that represent unique challenges in understanding the effects of environmental stressors on the health and resilience of complex biological systems.

Signature discovery in the fecal microbiome. Recent obesity and lipid metabolism studies show that bile acids have a significant role in the reduction of weight gain by a hormonal mechanism that is independent from caloric intake. It appears to include direct effects of bile acids on the gut microbiome, the relationship between which is dynamic. While conjugated bile acids inhibit the survival of certain microorganisms, other microorganisms are able to use them as a carbon, nitrogen, or sulfur source. Data from this project demonstrated that gastric bypass surgery changes the gut microbial ecology to reestablish a flora more similar to normal weight. The success of surgery also correlates well with the microbiota composition. This portion of the study helped to define the effects of surgery-related physiological changes on the host-microbiota and enhanced the current understanding of the role of microbiota on surgical weight loss and host energy balance.

Identification of systemic components associated with preconditioning induced protection against ischemic tissue injury. Collaborating with Oregon Health & Science University (OHSU), we established the OHSU-PNNL Co-Laboratory for Integrated 'Omics to tackle problems related to the functional proteomics in complex model systems. One such model system is the use of toll-like receptor (TLR) agonists to induce tolerance to ischemic injury in mouse models of brain, kidney, heart, liver, and lung ischemia. The Stenzel-Poore group at OHSU has shown that the combined induction of circulating factors and a local tissue response are required to mediate the protective effects of TLR agonists; however, the identity of these factors is currently unknown. We are currently providing a comprehensive global proteomics analysis of samples provided by the group to identify the TLR-mediated responses in the systemic circulation and in the brain that may orchestrate ischemic protection with the goal of new therapies for ischemic injury.

Quantification of brain sub-region neurotoxic dosimetry and response in juvenile rats. As climate change affects agricultural production, the use of pesticides is likely to increase, thus increasing the exposure of agricultural workers and their families to these toxic chemicals. Very little is known about the developmental aspects of organophosphate toxicity; thus, it is difficult to estimate the risk for the children of agriculture workers. This portion of the project used the unique nanospray desorption ionization imaging MS technique developed at PNNL to study to the localization and concentration of important neurotransmitters in the brains of juvenile rats that had been exposed to chlorpyrifos, a neurotoxic organophosphate. Spatial mapping of important neurotransmitters to specific brain regions was observed with high spatial resolution and sub-femtomole sensitivity.

Pilot study of regulatory feedback loops in cultured cells. Signal transduction networks convey information in cells by adding and subtracting phosphate groups from specific proteins. The highly sensitive, highly quantitative targeted MS techniques at PNNL were used to study the stoichiometry of phosphorylation to identify novel regulatory circuits that regulate cell growth in both prokaryotes and eukaryotes.

Plans for FY 2016 include using the gut microbiome as a model system for studying fundamental ecological processes that are responsible for restoring health microbial communities in the human gut after perturbation by diet, disease, or toxic exposures.

PN15016/2691

Increasing Annual Biomass Productivity Through Development of Cold Tolerance in Algae

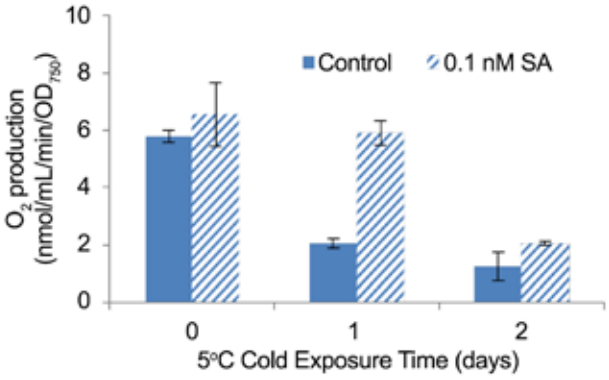
Michael H. Huesemann

We aim to understand the basic stress response mechanisms and methods to mitigate abiotic stress in photosynthetic organisms to increase photochemical efficiency, winter resilience, and biomass growth in bioenergy feedstock crops in temperate regions of the continental United States.

Algae have the potential to provide carbon-neutral biomass for the sustainable generation of fuels and industrial products. Cold stress severely inhibits growth in algae, similar to many highly productive tropical biofuel crops such as sorghum and sugarcane. Mitigating the damage to the photosynthetic apparatus from cold exposure can improve resilience of photosynthetic organisms and enhance cold season biomass productivity. Specifically, cold stress in photosynthetic crops is especially relevant in the continental United States due to the high latitudes and seasonally cold climates.

Our research project explored methods of improving cold tolerance in photosynthetic algae specifically through applications of the plant stress hormone2-hydroxybenzoic acid (salicylic acid [SA]), which has surprising effects on the systemic enhancement of cold tolerance in several distinct genera of crop plants like tomatoes, cucumbers, and rice. Although it is well known that winter conditions severely reduce biomass productivity in algae, the current literature on enhancing cold tolerance in algae is negligible as is the current literature on the effects of SA on algae.

SA was hypothesized to have analogous actions in green algae (Chlorophyta) as in higher plants. The protective mechanisms of SA are not fully understood, but there is a general consensus that it behaves as a global signal for defense gene expression. This defense mechanism gives terrestrial plants what is known as systemic acquired resistance against pests and pathogens. As a part of this response mechanism, plant cells upregulate stress response networks that, among other actions, provide added capability to dissipate reactive oxygen species (ROS) generated by excess light energy. This ability to quench damaging reactive molecules is the mechanistic hypothesis of cold tolerance enhancement in crops plants and, in this study, algae.



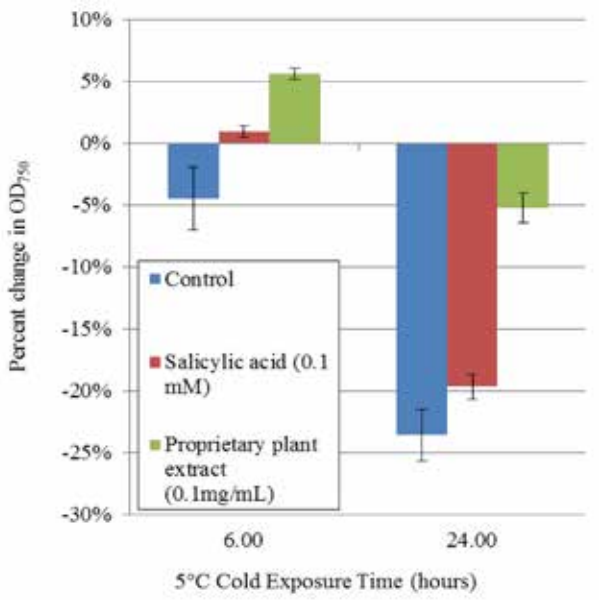
Effect of SA on photosynthetic oxygen production under cold stress in Scenedesmus obliquus DOE0152.Z. Relative to the control, photosynthetic oxygen production under cold stress declined much slower in the presence of SA, indicating a protective effect of this stress hormone.

Our objective was to test SA as an exogenously applied stimulant to enhance cold tolerance in algae. We initiated an assessment of cold tolerance in microalgae currently being evaluated as potential commercial biomass crops. We determined the optimum concentration of SA for the alga *Scenedesmus obliquus* DOE 0152.Z by measuring the rates of photosynthetically derived oxygen production under cold stress over a concentration gradient of SA (0.01 to 10mM). We demonstrated the significant protective effects of 0.1mM SA on *S. obliquus* DOE 0152.Z in maintaining the activity of oxygenic photosynthesis under conditions of cold stress over several days. Interestingly, the observed protective effects of SA were only temporary under cold stress conditions. To explore in greater detail the potential of SA on increasing growth rates during cold-season algae production, the optimum concentration of SA (0.1 mM) was used in a laboratory-based, cold-weather climate simulation of pond water temperatures in Tucson, AZ measured during early spring. No statistical difference in the growth rate was found between the control and 0.1 mM SA treatment. SA had definitive protective effects under cold stress conditions but failed to improve the biomass productivity of treated cultures. Although there may be protective effects of SA on oxygenic productivity, observations

PN15032/2707

indicated that under the tested conditions, there was no significant enhancement of the growth rate or long term cold tolerance of the alga.

To explore cold tolerance further, we developed a novel rapid cold tolerance test (RCTT), which enables high throughput screening of bioactive compounds on the growth and resilience of algae cells under cold stress environments. We increased our processing capability by leveraging microplate-based assays to screen for compounds that enhance biomass productivity under cold conditions in photosynthetic algae. Using the RCTT, a plant extract of proprietary composition was discovered that has cold tolerance enhancing effects greater than those observed in SA. Further tests will elucidate if this compound will increase the biomass productivity under a cold weather climate simulation. Our screening methodology is applicable to exploring the roles of other plant hormones and biostimulants under a myriad of abiotic or biotic environmental stressors such as heat, salinity, light, parasites, and predators. The ability to screen algae for environmental stress resilience provides a foundation for future efforts in optimizing not only microalgal biofuels but also photochemical and carbon fixation potentials of other photosynthetic processes.



Quantifying cold tolerance in the RCTT: Percent change in biomass concentration (optical density at 750 nm) of S. obliquus as a function of cold exposure time (5°C and light intensity of 500 µmol photons/m²/sec) in the presence of SA and a proprietary plant extract relative to an unamended control. Six hours of cold exposure reduced the biomass concentration in the control, while the SA and plant extract amended cultures continue to grow slowly. Even after 24 h of cold exposure, biomass concentration in the plant extract amended culture declined only 5%, compared to 24% in the control.

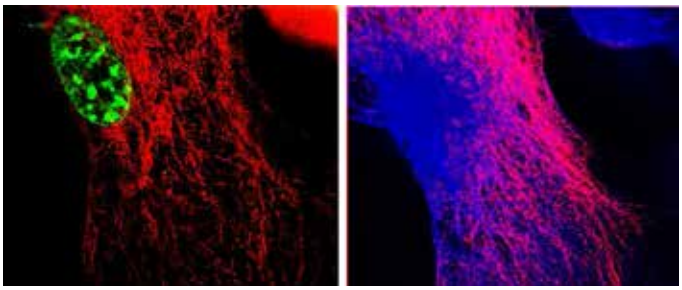
Microbial Community Dynamics and Plant Phenomics with Single-Cell Gene Expression and Imaging Mass Spectrometry

Galya Orr

We are developing a novel approach to quantify the expression of multiple genes or proteins in individual bacterial cells using mass spectrometry approaches.

The inherent heterogeneity of microbial communities limits the questions that can be resolved by averaged cell population measurements, which lump the behavior of an entire population of cells or organisms into a single average value. It is possible that the processes deduced from the average are not actually employed by individuals within the population. To this end, mass cytometry has been used to analyze single cells labeled by antibodies tagged with rare earth elements, mostly to detect the expression of specific cell-surface receptors in mammalian cells. However, no study has yet applied mass cytometry to quantify multiple mRNA species in single cells using an *in situ* hybridization approach in high throughput. Generation of *in situ* hybridization probes and their application in microbial cells and communities has been well established using fluorescence methods and widely used as a mainstream approach by us and many other groups.

The goal of this project is to establish new approaches using existing EMSL instruments to enable the investigation of individual cells within complex cell populations. Two specific aims will be pursued: first, we will establish a novel approach using the CyTOF to quantify the expression of multiple genes in individual cells from complex microbial communities in high throughput. This method will be used to understand the metabolic and regulatory principles underlying the function of the community as a whole. Under the second aim, we will establish a novel approach using the NanoSIMS to image plant tissues and their colonizing microbial communities *in situ*. This approach will be used to understand mass and energy fluxes and identify the critical players at the cellular and molecular levels with sub-micrometer spatial resolution. The novel approaches will also be applied to decipher interactions underlying the function of complex microbial communities in C cycling, biomass degradation, plant resistance, and the release of volatile organic compounds.



Effect of SA on photosynthetic oxygen production under cold stress in Scenedesmus obliquus DOE0152.Z. Relative to the control, photosynthetic oxygen production under cold stress declined much slower in the presence of SA, indicating a protective effect of this stress hormone.

Based on our solid experience in the design and application of fluorescence *in situ* hybridization (FISH) probes, we designed multiple probes and established the approach for tagging them with different rare earth elements, relying on multiple sub-probes (~20 bases each) spaced along the mRNA molecule by 3–5 bases. Each sub-probe is tagged with 20 atoms carried by the commercially available metal-chelating polymers. We established the protocol for reacting the maleimide groups on these polymers with SH groups that we added to each sub-probe. This approach ensures that each probe is tagged with sufficient number of atoms for mRNA detection and quantification using both the CyTOF and the NanoSIMS.

Using the CyTOF, we optimized the above tagging approach and demonstrated the detection and quantification of the probes in bacterial cells with no detectable background. In the coming year, we will establish the application of the technique to detect and quantify the expression of multiple mRNA species in a single bacterial cell. Using the NanoSIMS, we optimized immunostaining protocols in mouse alveolar epithelial cells grown in culture. Using an antibody specific for actin, followed by a secondary antibody tagged with CdSe quantum dots, we were able to acquire chemical images with a resolution and accuracy comparable with fluorescence images of the same cell taken by super solution fluorescence structured illumination microscopy. We started developing the protocols for applying this approach in bacterial cells.

It is anticipated that the new capability from this project will be applied to decipher interactions underlying the function of complex microbial communities in C cycling, in biomass degradation, plant resistance, and the release of volatile organic compounds. Initially, the new approach will be applied to achieve a mechanistic understanding of the carbon cycle in the terrestrial ecosystems with a focus on processes that take place in the rhizosphere, where interactions within and between complex microbial communities and roots directly impact C cycling.

PN15092/2767

Microbiome Models Across Scales - From Metabolism to Succession: A Framework for Modeling, Simulation and Theory Development for Microbial Ecology

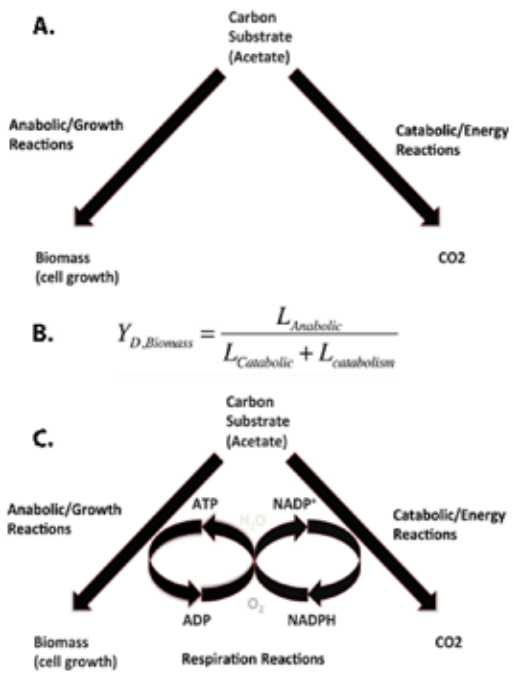
William R. Cannon

We are developing new computational and theoretical methods that are more predictive than the current state of the science to allow the understanding of adaptation, acclimatization, and collapse of microbial communities in a changing environment.

Predictive modeling relies on solving differential equations in which the necessary equation parameters are either based on first principles or empirical data. This process has hampered predictive modeling of biological systems in that the relevant scales (such as those in metabolism) are too large and complex to be modeled by first principles, and the necessary rate constants are simply not available. This project is modeling the dynamics of microbes in complex environments, soils, and the gut to understand how a changing environment affects the microbes residing in it and how these microbes feed back to and shape the environment. We are developing the methods and software designed to simulate large-scale microbial communities, integrate metabolomics and proteomics data, and subsequently understand microbial ecology on a fundamental level.

To commence the project, we evaluated the sufficiency of using functional guild models of microbes to represent metabolic capacity of the microbe metabolism and subsequently developed a more flexible method. The traditional approach to modeling function guilds of microbes attempts to model a functional capacity of the metabolism of a microbe. Because microbe capacity is abstracted to a simple representation, these models are described as functional guilds rather than specific microbes. One functional guild type may represent more than one microbe or operational taxonomic unit (OTU).

In a traditional functional guild approach, the model consists of two high-level processes: energy supplying and growth modeling. In the energy supplying process, a nutrient with a high redox potential (usually a carbon compound) is oxidized to a compound with a much lower redox potential. This reaction provides the energy needed for an organism to grow. The organism grows by capturing a fraction of this energy and channels it into the growth process. As mentioned above, each "organism" or guild has a growth equation which also uses the carbon source for growth. The relationship between the energy supplying and growth processes is fixed by an experimentally measured constraint: the carbon yield, which is essentially the fraction of the nutrient used for growth relative to the amount of nutrient used for growth and energy supply. While this is convenient for many purposes, microbes in a changing environment have variable yields that reflect the conditions of their environment.



A) Functional guilds are usually modeled as an anabolic or growth reaction competing with a catabolic or energy supplying reactions. B) This results in a fixed yield: the amount or likelihood of biomass produced per carbon-based nutrient consumed. C) Our hybrid model incorporates respiration reactions that allows for the yield to vary according to the environmental conditions.

We developed a hybrid approach to functional guild modeling that does not require a fixed yield to relate the energy supplying process to the growth process. We do this by requiring the energy supplying process to pass the chemical energy on to an intermediate energy carrier that can be used either directly or indirectly by the growth process.

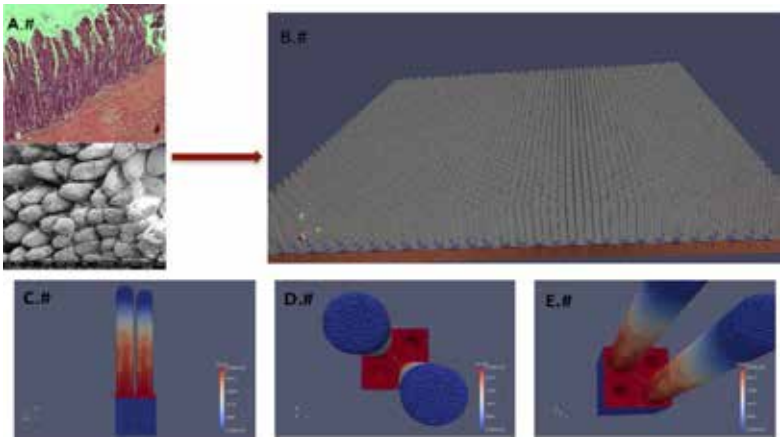
PN15069/2744

The addition of these energy carriers matches how metabolisms of organisms actually work: they store energy in high potential intermediates such as NADH, ATP, GTP, flavonoids, quinones, and other chemicals. These high potential intermediates are then used to drive the growth processes of cells. In fact, the ability to expand these models as needed – from simple models of functional guilds to full genome-scale models of metabolism to address specific scientific questions – was one of three goals for these models. Our other requirements for these models is that the representative equations be based on physics (thus providing predictive dynamics) and that the code be amenable to high performance computing so that the microbes could be modeled in complex environments. This work is still in its early stages, but we have built the first generation of models for fermentative organisms, methanogens, and acetogens.

Simultaneously, we have been developing the model of the environment of the microbes. The environmental model combined with the functional guild models will comprise the model of the microbiome. Our first environmental model is that of the human gut, in which we will model the effects of radiation. While we intend on also modeling soil microbiomes, the gut environment is a much more structured, improved characterized environment making it a better target for our initial efforts.

Our gut model was developed in collaboration with a gastrointestinal surgeon and biophysicists at the University of Chicago and is based on an earlier 2D model SEGMEnT. We developed the initial work into a full 3D model in the Biocellion software framework, including physical structures (villi and crypts) and a number of different cell types modeled as individual agents such as enterocytes, intestinal stem cells, undifferentiated transit amplifying cells, and differentiated enterocytes. The cell types undergo differentiation based on cell signaling pathways that are included in the model and thus allowing for morphogenesis and apoptosis. As the cells grow, they push and shove each other by physical contact.

In the next year, we will be working to create the functional guild models of a microbial community with the gut environmental model that includes mucin. Mucin is the network of complex carbohydrates in the gut (excreted by goblet cells in the epithelium) on which microbes reside. Our long-term goal is to model radiation effects on the gut microbiome and how radiation impacts the host.



Model of the gut epithelium that serves as an environment for microbial communities. It is based on initial work at the University of Chicago but has been ported to Biocellion for high performance computing needs.

Microbiome Responses to Hydrologic Regime Shifts and Subsequent Alteration to Ecosystem Function

Vanessa L. Bailey

We are determining how hydrologic change impacts the coupling of soil biogeochemical cycles and whether there are broad rules that transfer between ecosystems. Understanding these processes under changing hydrologic regimes is critical to improving process-rich models of climate change effects on the land-climate system.

Soil microbiomes strongly influence the functioning of terrestrial ecosystems from the pore-scale to the global-scale by transforming materials in the environment. For example, research shows that the availability of water strongly influences the rate and nature of microbiome-driven material transformations. Soil water content is a dynamic variable influenced by shifting hydrologic regimes due to natural variation (e.g., seasonal and weather-driven precipitation) and human influences (e.g., land use and climate change). Determining how soil water content dynamics and its changes impact soil microbiome composition and function is fundamental to DOE missions related to global carbon and water cycles.

This project seeks to discern the sensitivity of soil microbiome molecular processes to altered hydrologic regimes. Filling this knowledge gap is critical, as it currently limits our ability to predict changes robustly in ecosystem function as a consequence of altered hydrologic regimes. We aim to fill the knowledge gap through hypothesis-driven experiments coupled to multi-'omic characterization and stable isotope probing of key metabolic pathways. Changes in the mean and temporal variability of soil moisture will alter the balance among aerobic and anaerobic metabolic pathways, but underlying dynamics of soil microbiome functional potential are currently unknown. We hypothesize that rapid fluctuations in soil moisture will depress aerobic respiration and iron reduction by decoupling microbiome 'omic profiles and elevate rates of sulfate reduction – and therefore depress methanogenesis – by promoting *in situ* sulfur recycling.

Tidally influenced wetland near (A) the mouth of the Columbia River and (B) the Caribou-Poker Creeks Research Watershed LTER.

Aquatic-to-terrestrial transition zones are biogeochemical hot spots that provide key ecosystem services ranging from carbon storage to contaminant mitigation to sediment stabilization, while also releasing CO_2, CH_4, and N_2O to the atmosphere. These environments have significant effects on larger-scale functioning, but their ecosystem services are threatened by factors driven by shifts in hydrologic dynamics. The microbiome response to altered wetting-drying dynamics will strongly influence the functioning of aquatic-terrestrial transition zones. Changing precipitation patterns and a warmer climate are altering the magnitude and dynamics of hydrologic flow, both of which significantly impact biogeochemical functioning in these zones at local, regional, and global scales.

Our research focuses on two different ecosystems, each subject to significant hydrologic stressors. The first is a tidally influenced wetland near the mouth of the Columbia River in Washington State. Climate change is altering the hydrologic regime in this and similar watersheds such that historically snowmelt-driven moisture inputs are being replaced by rain events, and the timing of snowmelt and precipitation is changing. The consequences of these shifts yield changes in the soil stability and timing/magnitude of water runoff and material fluxes in the Columbia River Basin. The second site is a permafrost zone within the Caribou-Poker Creeks Research Watershed, a long-term ecological research site near Fairbanks, Alaska. Permafrost in boreal forest is at risk of thaw due to the increased frequency of fires and climate change that can rapidly shift the ecosystem from permafrost-dominated to -free.

Both locations were sampled in 2015, and wetland soils and permafrost cores will be subjected to altered hydrologic regimes in highly controlled laboratory experiments that control the soil water content, fluctuations in water content, and the local redox state. These conditions will force shifts in the microbial access to different terminal electron acceptors that will be reflected in biogeochemical measurements. These observed changes will be evaluated with the genomic information regarding the potential of the soil microbiome to mediate processes, the expression of these processes in the proteome, and the outcome of these processes in the metabolome.

PN15078/2753

Microbiome-Exposome Interactions

Brian D. Thrall

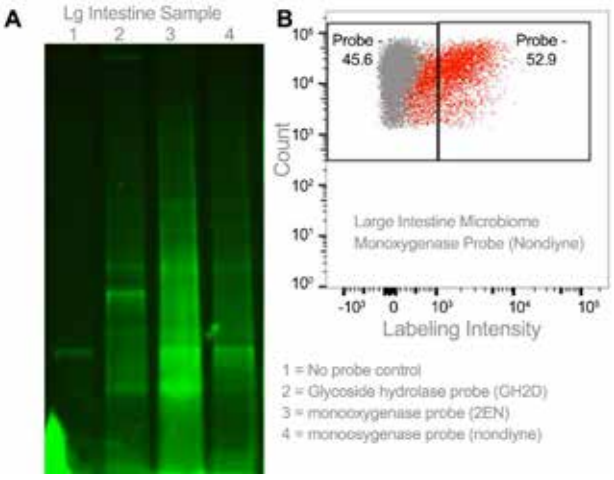
This project is addressing key gaps in our understanding of how the composition and function of mammalian microbial communities (microbiomes) are impacted by exposures to environmental agents and how these impacts host susceptibility to the agents.

The broad diversity of microbes residing in the body greatly extends the synthetic and metabolic capacities of the human genome through the production of essential amino acids, vitamins, metabolism of dietary chemicals, and shaping patterns of host immunity and tolerance. Emerging studies also show that the diverse metabolic functions encoded by trillions of microbes within the intestinal tract can mediate the chemical transformation of xenobiotics, such as pharmaceuticals and environmental contaminants associated with energy production. Still, the impact that environmental exposures have on the microbiome, and in turn how perturbed microbiomes influence host susceptibility to environmental agents, is poorly understood, largely from the lack of understanding of the enzymatic activities and metabolic pathways involved, and the microbes that express these. To advance our understanding of the metabolic functions of microbiomes, innovations in analytical approaches are needed that permit the identification of the specific proteins associated with a given biochemical activity.

Through the introduction of activity-based probes (ABPs) and proteomics profiling coupled with new computational approaches for prediction of microbiome functions, a central goal of this work is to advance microbiome research beyond current metagenomics strategies to achieve a mechanistic understanding the specific protein and metabolic activities that comprise a given microbiome phenotype. This goal is being achieved through three interrelated aims: determining the impact of environmental exposures (radiation, chemicals) on the composition and diversity of gut microbiomes using mouse intestinal microbiomes as a model; developing and applying ABP profiling (ABPP) methods to enable identification of proteins that have metabolic activity toward foreign chemicals (xenobiotics) and the microbes that express these activities; and applying emerging metabolomics technologies to test predicted consequences of perturbing microbiome compositions from environmental exposures on their metabolic capacity.

Within the 6 months of project commencement, significant progress has been made in optimizing sample preparation for the analysis of microbial communities, analyzing gut microbiome samples from mice exposed to different forms of ionizing radiation, and developing, synthesizing, and testing novel ABPs that report on targeted metabolic activities, including monooxygenases and glycoside hydrolases.

Impact of exposures on microbiome composition. Through collaborations with the University of Florida and Eastern Virginia Medical Schools, experiments were initiated to investigate impacts of different forms of external ionizing radiation on gut microbiomes in rodent models. Intestinal microbiome samples from mice exposed to therapeutic doses of gamma irradiation (0, 3, 9 Gy) were received, and the 16S sequence analysis is in progress to evaluate shifts in microbiome composition. In addition, samples were prepared from animals that were provided a metabolic intervention treatment consistent of amino acids and trace nutrients (Enterade™), which were previously shown to minimize toxicity to the intestinal epithelial tissue. Metagenome sequence analysis is currently in progress to evaluate the relationship between radiation-induced changes in the host environment and shifts in composition/diversity of the microbiome. In parallel, metabolomics analyses are in progress to determine changes in gut metabolites (including lipids



ABP of targeted microbiome metabolic activities: A) Protein gel showing different patterns of binding of ABPs following labeling reaction with microbiome of mouse large intestine; B) Example flow cytometry analysis of mouse large intestine microbiome after labeling with either no probe (control) or monooxygenase ABP.

PN15073/2748

involved in inflammatory pathways) to determine the effects of exposure and intervention treatment. As these analyses progress, we will integrate these approaches with measurements of metabolic pathway activities using ABPs described below to determine how perturbations of the microbiome composition by radiation influence its metabolic functions.

Activity-based proteomic profiling of microbiome metabolic activities. To enable identification of specific metabolic activities, proteins and microbial community members that express these, we are developing ABPs that target enzyme active-site chemistries for common xenobiotic metabolism activities. Our initial focus has been on the development, optimization, and testing of ABPs that target monooxygenases and glycoside transferases/hydrolases that represent major pathways of phase I and phase II metabolism of environmental chemicals (including drugs) known to be performed in host liver tissues by P450 and glucuronyl transferase enzyme superfamilies, respectively.

Design and synthesis of first generation ABPs has been completed, and we successfully demonstrated the ability of the ABPs to label (bind) proteins selectively within the large and small intestines of untreated mice, providing a first-time demonstration of *in vivo* labeling of specific microbiome enzymatic activities. Through the use of click-chemistry, we demonstrated that fluorophores can be conjugated to the probes after binding to target *in vivo* and used to sort microbes based on their targeted metabolic activity by flow cytometry. Initial 16-sequence analyses from ABP-sorted samples have also confirmed ABP binding to microbial components of the intestine. Thus, our early results provide proof-of-principle evidence for a new technological strategy that will enable rapid identification and isolation of specific microbial components (proteins, organisms) based on targeted metabolic activities. Ongoing studies include optimization of sample preparation methods and ABP reaction conditions to optimize throughput, selectivity and sensitivity of the approach. In addition, we PNNL computational biologists are developing a custom proteomic database that will be used in conjunction with the ABPs for proteomic identification of metabolically active microbiome proteins.

Future studies will use this new technological strategy to understand how specific metabolic functions of microbiomes are altered following environmental exposures and determine how these functional shifts relate to changes in microbiome composition. Because of the broad utility and adaptability of the activity based strategy, successful development of these tools and approaches will not only aid in understanding of the metabolic functions of mammalian microbiomes but also facilitate their broader application to more complex microbiomes in the environment.

Multi-Scale Processes Controlling Spatial Variation in Greenhouse Gas Emissions in a Subarctic Watershed

James C. Stegen

This project combines field measurements with simulation modeling to deepen our understanding of and reduce uncertainty in predicted greenhouse gas emissions across permafrost to non-permafrost transition zones.

Microbial communities play a central role in the functioning of natural ecosystems by heavily influencing biogeochemical cycles. A major scientific challenge is to use knowledge of those influences to improve the ability of Earth System Models to predict future climate change robustly by incorporating feedbacks between environmental change and biogeochemical rates. Understanding how shifts in the environment are tied to shifts in biogeochemical rates via changes in microbial communities is particularly relevant in high latitude terrestrial systems underlain by permafrost due to vast carbon stocks currently stored within thawing permafrost.

The primary objective of this study is to gain new knowledge of the factors that govern observed patterns in greenhouse gas emissions rates associated with permafrost to non-permafrost transition zones. We additionally aim to use that knowledge to improve the representation of soil microbiology in the Community Land Model (CLM). To pursue these objectives, field studies are being used to generate data needed to first test CLM predictions and in turn provide hypotheses for how the model may be improved through inclusion of additional biotic (e.g., microbial community composition) and abiotic (e.g., organic carbon composition) features. The field site near Fairbanks, AK is characterized by spatial transitions in the presence/absence of permafrost and in active layer depth (the depth of soil overlaying permafrost). Across these spatial transitions, greenhouse gas emission rates are being directly measured and biotic/abiotic features of the associated soil environment are being characterized.

From an initial sampling trip to the AK field site in fall 2013, CO_2 emissions were characterized across spatial gradients in active layer depth. Results show a strong relationship between active layer depth and CO_2 emission rates, but only across the lowest elevation sites with the thinnest active layer depths. This result points to a highly non-linear influence of active layer depth on CO_2 emissions at the landscape scale. Field sampling designs were implemented in the 2014 field season to characterize more effectively this non-linear relationship and understand how other environmental features contribute to the non-linear behavior.

Beyond the influence of active layer depth, soil cores were taken across the spatial gradients in active layer depth. Soil core material from 2013 was characterized in terms of numerous biotic and abiotic characteristics, including microbial community and organic carbon compositions. Soil cores from 2014 sampling are currently being processed using similar characterization methods; a portion of characterization is with EMSL. Coupling below-ground data and CO_2 flux from 2014 samples revealed that the relationship between active layer depth and CO_2 flux is indirect. The best predictor of flux rates—and presumably the variable that most directly indicates the control point over CO_2 flux—was a proxy for the degree to which soil C has been microbially processed. The relationship was much stronger than for other explanatory variables that were expected to have strong influences, such as temperature, moisture, and root density.

In addition to above-summarized activities, the single-site version of CLM has been set up, and initial simulations have been run for different permafrost conditions at our field site. Retrieving and formatting the necessary meteorological forcing data was a significant achievement, and the model setup can be used by other internal and external researchers.

The next modeling steps include a formal CLM spin-up with resulting model outputs used to characterize predicted-observed deviations between CO_2 emissions and soil C stocks. Additional above- and below-ground data will be used to interpret these deviations to identify processes and/or features missing from CLM. Multiple instances of CLM will be run, each corresponding to a specific spatial position within our field spatial domain. This approach will take CLM—a global-scale model often run on 10 km^2 grid cells—down to the scale of point field measurements, thereby reaching across an extreme disparity in scale. To support this integration, we quantified spatiotemporal variation in CO_2 emissions (using the 2015 field season to sample at a larger spatial scale relative to 2014) and net primary production.

Ongoing efforts associated with soil core processing will include characterizing vertical profiles of numerous key variables such as soil moisture, pH, texture, C content/composition, and microbial biomass, composition, and potential enzyme activities. These data will enable a multi-scale comparison between CLM predictions and empirical observations. In total, results have been presented at national and international meetings, formed the basis of an invited seminar, and are being used to generate three manuscripts for submittal during FY 2016.

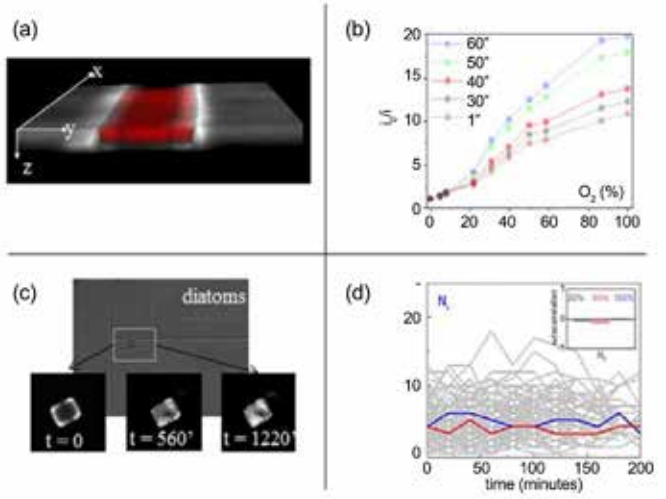
PN14027/2611

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

Andreas E. Vasdekis

This project investigates biofuel production at the single cell level: by treating cells as a single biochemical factory, biofuel production efficiency and timing will be measured precisely, hence unmasking better performing traits.

Our society's prosperity and growth is inevitably linked to reliable energy sources. From climate change, increasing energy demand, and finite fossil fuel reserves, sustainable prosperity and growth necessitate the use of renewable energy sources such as solar, wind, or biofuel. These are of key importance due to their compatibility with our current transportation infrastructure. Despite substantial advancement during the past decades, there remains a plethora of unknowns surrounding alternative energy sources especially within the context of efficiency and species selection or design. In this project, we are addressing such challenges by directly imaging biofuel synthesis at a controlled cell and molecule density down to the single entity. At this level, the cell acts as an isolated chemical factory while its synthetic performance can be precisely characterized, unmasking invisible spatiotemporal phenomena and improved performance.



(a) A SIL-enabled microfluidic channel, where red denotes a fluorescent dye solution in which the microchannel is infilled and grey denotes impregnated channel walls with oxygen-sensing dye; (b) sensor intensity response to oxygen as a function of oxygen concentration (x-axis); (c) an isolated diatom immobilized for >20 h while its intracellular protein kinetics are fluorescently monitored; and (d) the lipid fluctuations of single yeast cells immobilized in a sub-microfluidic trap.

The project's methodology is based on cell handling microsystems, chemical imaging of biosynthesis, and 'omic analyses (i.e., transcripotmics and proteomics) of such pre-analyzed microorganisms.

In FY 2015, we expanded on last year's activities, reaching primarily two milestones through work performed at both PNNL and the University of Idaho: photophysical characterization of 3D optical sensors in microbioreactors and investigation of microbial growth and metabolism in microfluidics. The work was collaborative, including academic partners at MIT (USA), EPFL (Switzerland), and the University of Idaho. For optical sensing, the focus was on oxygen, an element of significant implications, as it is one of the most important electron acceptors in bioprocessing. We implemented solvent immersion imprint lithography, enabling direct impregnation of planar polymer slabs with an oxygen-sensing chemical moiety. This approach enabled two unique characteristics. The first was simplicity, requiring simple benchtop processing based on widely available organic solvents. The second unique element was the ability to impregnate a 3D distribution of sensing moieties, including independent control of sensor sensitivity and dynamic range. This work was prepared and the manuscript submitted at the end of FY 2015, with a U.S. patent application also filed.

For cell physiology and growth in microfluidics, previously published single-cell isolation methods (from FYs 2012 to 2014) were implemented to demonstrate the applicability of such assays in single-cell immobilization for prolonged periods to explore intracellular events and growth. Regarding the former, we demonstrated diatom immobilization with PNNL at Sequim, WA as well as single bacteria trapping. Such cell types were successfully immobilized for over 12 h. Specific to diatoms, the biosynthetic properties were monitored via fluorescent imaging of intracellular protein kinetics. For cell growth, a proof-of-concept investigation involved Shewanella and showed that such demanding strains grow under microfluidic isolation, indicating that physiological conditions are characteristic of these assays.

Our focus in FY 2015 was on the oleaginous yeast *Yarrowia lipolytica* (work performed in collaboration with MIT and the University of Idaho). Specifically, the project expanded on the aforementioned deliverables to image the synthesis of biofuel precursors directly in the form of neutral lipids at the single cell level. To this end, one journal article has been published in *Metabolic Engineering*, another manuscript will appear in the *Journal of Polymer Science Part B: Polymer Physics*, and a third article is being submitted to a journal as of the end of FY 2015.

PN12005/2406

Rapid Viability Assays for Biothreat Event Characterization

Janine R. Hutchison

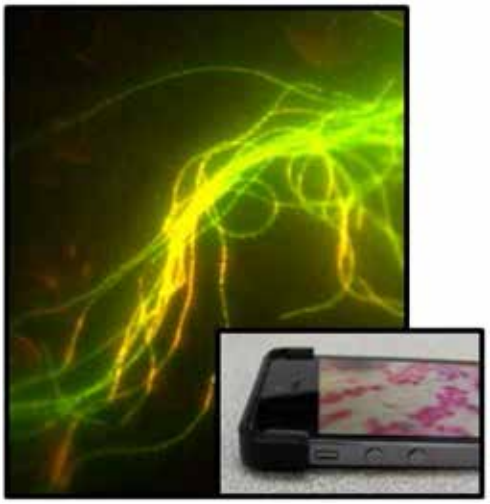
This project uses PNNL's expertise in bacterial detection and analysis to develop a field-based method to assess bacterial viability (is the sample alive or dead?) and the associated threat (will this cause disease?) of unknown environmental samples.

The identification of bacterial pathogens in environmental and clinical samples is important for a variety of environmental, national security, and medical applications. The response to a biological threat hinges largely on the knowledge of whether an identified organism can grow and subsequently cause disease (i.e., its viability status). As this information will guide the proper response and remediation, the time to detection and characterization is a critical parameter for protecting lives and containing exposure. While methods to detect and identify biological agents have been effective, significant challenges still exist in the follow-on determination of the biological threat agent's viability. For example, detecting DNA in an unknown sample can reveal the identity of the organism (such as *Bacillus anthracis* vs. *Yersinia pestis*), yet this identification does not provide indication of the organism's viability and therefore its potential to cause disease.

Rapid knowledge of the viability status of an unknown sample would greatly enhance downstream response and actions during remediation and recovery. Current viability methods rely on a laboratory-based cultivation step that takes hours delaying decisions made during a threat scenario. In this project, we will enable field-based detection for first responders and scientists to assess threats during a biological threat. Specifically, our project is focused on evaluating bacterial viability methods for *B. anthracis* and *Y. pestis*. The aims of this effort include the development of rapid (<60 min) viability assays for bacterial spores (*B. anthracis*) and bacterial cells (*Y. pestis*), and the subsequent integration of these assays into biological detection technologies with the end goal of rapidly characterizing biological threat events to inform both response and recovery.

To accomplish our goals, we are using three different approaches that can be coupled. Our first approach is based on the premise that DNA within non-viable cells can be specifically altered via chemical treatment. This technique allows for the selective detection of viable bacteria via downstream DNA-based analyses. As modified DNA in dead cells cannot be amplified, any DNA detected post-treatment must have originated in a viable cell. The second approach maximizes the differential permeability of live and dead cell membranes. We coupled fluorescent cell staining with microscopy (traditional and smartphone-based) to identify organisms via specific molecular markers and differentiate live vs. dead cells. An unexpected outcome has been development of a 3D printable smartphone microscope. The PNNL design is unique in its low cost and disposable nature of the device. The final approach builds on our past work in the areas of rapid bacterial culturing. This experience enabled us to identify optimized growth and germination conditions to reduce overall detection time four fold.

We also developed and optimized a rapid growth and optical detection method for *B. anthracis* spores. A microfluidic incubation device was developed for the germination and imaging of spores. Low numbers of spores (50 to 5,000) are seeded into the chip in germination medium. The spores are allowed to grow and form filamentous vegetative cells that are then detected using PNNL smartphone microscopy, which is easily converted to a fluorescent microscope for improving its utility for imaging bacteria that have been stained with live-dead fluorescent dyes.



B. anthracis spores are germinated and stained to reveal the metabolically active filamentous vegetative cells. Using the PNNL smartphone, fluorescent microscope samples can be viewed and imaged quickly and easily.

During or just after the end of FY 2015, a manuscript based on our work from this project was published in the journal *Analyst*. A second article that describes our results of using biochemical assays to assess *B. anthracis* and *Y. pestis* and viability was accepted to the *Journal of Bioterrorism & Biodefense*. A summary as part of a larger article appeared in the *Domestic Preparedness Journal*, and a layman's summary based on some of this work newly appears in the online publication *Atlas of Science*. Overall, the work generated from this project provides additional methods for the detection and characterization community and enhances our ability to respond to a biological threat.

PN14035/2619

RhizoControl: Does the Rhizospheric Microbiome Influence the Plant Metabotype? A Plant Gnotobiotics Approach

G. Christer Jansson

We are building a knowledge base to understand how the rhizospheric microbiomes in the grass Brachypodium distachyon (Brachypodium) control the synthesis of volatile organic compounds (VOCs) and other metabolites and how these interactions affect drought tolerance in the plant.

Understanding plant-microbe interactions and their impact on plant metabotypes is highly relevant to DOE's missions in sustainable biofuel production, understanding carbon cycling, and mitigating negative effects of climate change. The knowledge is further of importance to a new EMSL focus on plant phenotyping, where the plant microbiota and their interactions with the plant host are of central interest. Many studies in the last decades have shown that plant-microbe interactions are key for understanding plant growth and health but also for sustainable crop production. There is growing evidence that a significant number of plant metabolites are in fact produced by associated microbes or through interaction with their host. However, a thorough investigation of plant-microbe interactions in plant metabolite profiling is lacking, which indicates a knowledge gap that constitutes a critical limitation in our ability to improve plants for renewable energy and chemicals production.

Brachypodium distachyon (Brachypodium)

The purpose of our project is two-fold: first, to establish the workflow and infrastructure for plant gnotobiotics work, and second, to employ the gnotobiotics approach in gaining understanding for if and how the rhizospheric microbiome influences and controls the synthesis of plant metabolites, including VOCs (i.e., its metabotype). The study was performed with *Brachypodium distachyon* (Brachypodium), a genomic model for bioenergy grasses like miscanthus and swithsgrass.

As an initial phase of establishing a plant gnotobiotics station, we are setting up four gnotobiotic isolators equipped with a stainless steel atomizer for sterilization of the interior. Transfer of plant material and other supplies from biohood to isolators will be performed with sterilizing cylinders that dock to the isolator via transfer ports. Once set up on tables, the isolators will be supplemented with light banks. VOCs will be captured from the efflux port and collected until analysis. While waiting for the isolators to be functional, we used single-plant containers. Seeds of the diploid inbred Brachypodium line also used for the reference genome were surface-sterilized, rinsed, and pregerminated on filter paper in sterile moist chambers to ensure their fertility and germinability. Germinated seeds (three seedlings per pot) were transferred after 7 days under sterile conditions to vented containers with a mixture of repeatedly autoclaved clay and vermiculite (3:1). Seven replicate pots were amended with a natural microbial community extracted from soil slurry were prepared. Filter-sterilized slurry extracts were added to a similar amount of control pots, which allows exclusion of non-biological or chemical differences between the two treatments resulting from the soil slurry application. This method also excludes impacts on physico-chemical soil properties that would occur by simply autoclaving or gamma-irradiating soil. A similar set of replicate pots with and without an added natural soil microbiome were set up as plant-less controls for VOC analyses.

The soil for slurry preparation consisted of four subsamples collected from a field site at the Washington State University Tri-Cities in Richland, WA in July 2015. The soil texture was classified as fine sandy loam with clay content of 7%, an organic carbon content of 0.43%, and a near-neutral pH of 7.6. Sterility controls of seed surfaces and soil slurry filtrates were performed on nutrient agar. Plant containers were placed in a randomized complete block design into a growth chamber under a 16:8 h (light:dark) photoperiod at 23°C and a relative humidity of 65%. Watering was done under sterile conditions, usually at 7-day intervals. When plants were

PN15089/2764

4 weeks old, leaves, roots, and rhizosphere soil were harvested for further analyses. Different treatments were encoded using abbreviations indicating: 1) plant (Bd) or control (C), 2) with or without soil microbiome (microbiome-plus, microbiome-minus), and 3) independent replicate pot.

To determine if there were any differences in the metabotype between plants grown in the presence (microbiome-plus) or absence (microbiome-minus) of associated rhizospheric microbiome, we analyzed samples from Brachypodium shoots with Fourier transform ion cyclotron resonance (FTICR) to obtain metabolomic fingerprints of the shoots. The results from the multivariate analysis demonstrated that the plant metabotypes clearly differed between microbiome-plus and microbiome-minus plants. Additionally, a principal component analysis (PCA) was performed to the same metabolomic dataset. Case plot of the PCA showed clearly that both groups of plants (microbiome-plus and microbiome-minus) are separated in the multidimentional space, also showing different metabolome composition.

Constitutive emission of VOCs from grasses is usually low but increases in response to stress. The first step in this task was to develop protocol and experimental setup for detecting and identifying VOCs emitted from Brachypodium. Four-week old plants were grown in small plastic containers. Ambient air entered the containers through a filter situated on the lid and specially designed to stop any microbes that would be found in the air. Similar containers with the same amount and kind of soil were used as control.

In one set of experiments, we used a solvent to trap the VOCs from the plants, which were enclosed such that only the leaves were inside the bag. Ambient air could enter the bag at the bottom of the bag, and air was extracted at the top. The extracted air was first passed through a cooled stainless steel tube to trap the water, and then passed through chloroform. The experiment ran for 15 h at a flow rate of 27 ml/min. Obvious peaks could be distinguished from the background, suggesting that this approach is a possible way for analysis.

While refining the technique for VOC detection from Brachypodium and prepare for comparison between Microbiome-plus and Microbiome-minus plants, we also need to acquire good reference libraries to identify the VOCs. Using currently available (but rather old and insufficient) libraries, we could identify nonadecanoic acid, benzoic acid, quinoline, carbazole, trimethylsilyl ester, glucopyranosiduronic acid, quinolinedione, phenethylamine, and dihydroxymandelic acid among the VOCs emitted from the Brachypodium.

In FY 2016, we will continue installation of gnotobiotic isolators and convert a section of a laboratory to a plant gnotobiotic station. Using the gnotobiotic facility will allow more controlled experiments and with a larger number of plants. Once the data from the metabolomic profiling and amplicons, metagenomes, and metatranscriptomes analyses are at our disposal, we are in position to interpret the results from the initial pilot studies and plan follow-up experiments using Brachypoidum plants with a demonstrated diversity in drought tolerance. We have currently 12 such Brachypodium accessions in the laboratory and have access to an additional 40 lines.

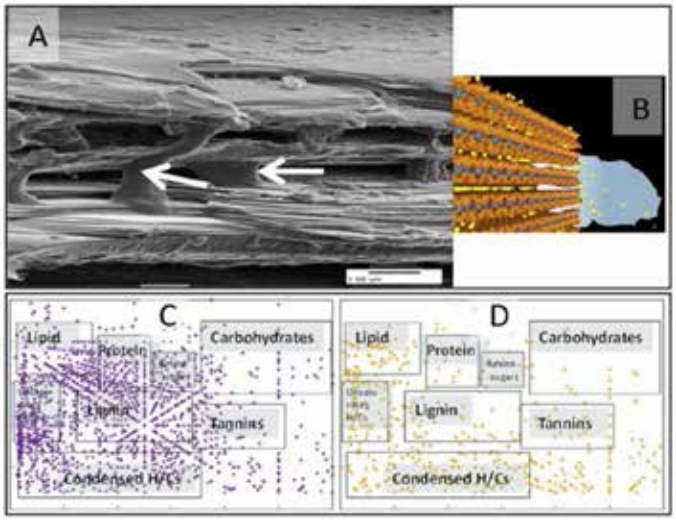
Rhizosphere Underground: Unraveling the Role of Microbes in Stabilizing Carbon Pools in Soils

Alice C. Dohnalkova

This project is developing a multi-capability platform for correlative imaging and analyses to investigate microbial and mineral association and interactions in the rhizosphere that will be applicable to a variety of environmental sciences systems.

Microorganisms are fundamental to biogeochemical processes, as microbial metabolism significantly contributes to the regulation of global carbon and nitrogen cycling. The zone immediately surrounding the plant roots, rhizosphere has an important role in the production and stabilization of soil organic matter, with considerably more abundant microbial population than in the adjacent bulk soil environment. However, the impact of the community of soil microbes within the rhizosphere has not been examined in detail due to the difficulty of tracking microscale processes in natural microbial communities in complex soil habitats.

This platform will be used on a model ecosystem to identify interactions of individual microcosm components: roots, soil fungi, microbial communities, and soil minerals. Special emphasis is given to formation of microbial extracellular polymeric substances (EPS) that may significantly contribute to recalcitrant pools of microbial products with mineral surfaces and as organic matter (SOM). In particular, we will examine the current hypothesis that preferential association with mineral surfaces and soil pores is an important mechanism of carbon sequestration. Our imaging approach will provide fundamental high resolution 3D information that will contribute to a better understanding of the factors influencing carbon flux and C sequestration toward the scheme of microbial carbon pump in soils.



A – An SEM image of biotite and microbially produced carbohydrates moving into its layers; B – A model of extracellular polymeric substances between the phyllosilicate layers; C and D – Van Krevelen diagrams of SEM compounds extracted by water from rhizosphere and bulk soil.

Seedlings of *Pinus resinosa*, a widespread North American pine forests ecosystem, was cultivated under experimental conditions in well defined soil mineral mix (quartz, biotite, and anorthite) with bacterial inoculum to develop biofilms-minerals associations. The mesocosms were destructively sampled at time points and investigated through the suite of imaging and analyses for extracted labile and persistent SOM. Datasets were correlatively evaluated, and a mechanistic model will be created from the integrated data that will connect microbial function to ecosystem processes.

We designed a multi-modal, multi-scale imaging and analytical system to provide an integrated workflow with seamless consecutive steps in multi-scale investigations from micrometers-scale to atomic level in imaging or to the respective resolution limits of coupled chemical analyses, including confocal microscopy for identification of biofilm-rich areas for electron microcopy, EMSL's state-of-the-art high resolution suite for microbial-mineral interactions visualization and analyses as well as micro-XRD for mineral analysis. We are coupling imaging with extractions of root microbial system for FTIR-MS to identify carbon species involved in the process.

During FY 2015, we applied this platform to addressing specific hypotheses in the *Pinus* sp. ecosystem. Specifically, the FTICR showed spatial differences in the rhizosphere soil systems. We observed a pattern in preferential bacterial attachment and coverage to a minerals. In addition, micro-XRD revealed differences in minerals with time, which suggested microbially induced minerals weathering. We also extracted DNA and anticipate the sequencing results to identify the key microbial players in the rhizosphere processes of mineral weathering and soil formation. The work from this project was presented at two international conferences during this year, one of which had an accompanying journal publication in *Microscopy and Microanalysis*.

PN14081/2665

Signatures of Environmental Perturbation – Microbial Community and Organic Matter Resilience

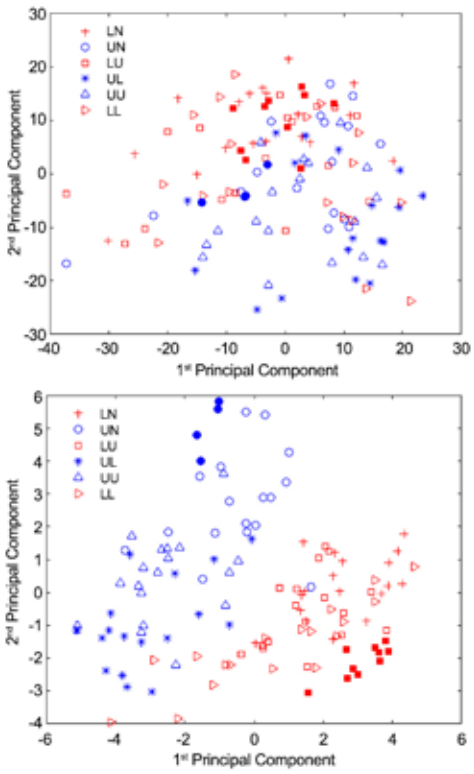
Vanessa L. Bailey

We are using existing capabilities to discover one or more signatures that indicate impaired resilience of the soil carbon biogeochemical system following a system-wide perturbation such as simulated climate change.

The microbial metabolism of soil carbon leads to the release of greenhouse gases that directly impact global climate by exerting a strong positive feedback effect on temperature (i.e., global warming). Analytical tools currently do not assess the vulnerability of soil carbon reservoirs to changing climate conditions, but it is likely that microbial metabolism of soil carbon increases with temperature, resulting in even greater emissions. The structure and function of the native microbial community is intimately linked to soil carbon by the deposition of new soil carbon and respiration of existing soil carbon as part of the terrestrial ecosystem carbon cycle. By integrating key chemical and molecular signatures of the soil system, microbial community interactions with the vulnerable soil carbon reservoir may be predicted with molecular resolution.

Ecosystem stress from pollution events and climate change are relevant topics to multiple federal agencies as researchers and policymakers strive to understand the ecosystem consequences of climate change. Successful development of chemical and molecular profiles that link soil microbiology with soil carbon to determine vulnerability and resilience would have a great impact on soil ecosystems assessments in response to global climate change. These integrated signatures could be used to support sustainable agricultural and food/energy crop security practices. In this project, we have been improving our understanding of soil biogeochemistry, ecology, and the relationships between carbon chemistry, microbial community structure and function, and ecosystem perturbations. The demonstration that our analytical tools can be integrated to identify signatures in a complex system such as soil has the potential to transform classical ecological research.

We have been leveraging an existing long-term experiment at the Arid Lands Ecology Reserve in Richland, WA in which soil cores were reciprocally transplanted between the cooler, moister upper slope position and the hotter, dryer lower slope position in 1994. This transplant was designed to mimic the stress of climate change with natural temperature and moisture gradients provided by elevation. A previous study of these soils has suggested that one of these core soils has lost robust microbial community function as a result of this transplant. A major goal in 2015 was to identify soil organic C process signatures that could separate our soil treatments, specifically the native soils from the lower and upper sites (LN, UN), the control soils at each site (LL, UU), and the lower-to-upper (LU) and upper-to-lower (UL) site transplants.



PCA plots for the FTICR-MS features of the soil samples. Top: for all features showing no discrimination of soil types; Bottom: obtained through the recursive application of 25 classification trees (425 features. The legend identifies symbols as Lower Native (LN), Upper Native (UN), Lower to Upper (LU), Upper to Lower (UL), Upper to Upper (UU), and Lower to Lower (LL) soil samples. Filled symbols are used to identify replicates.

The chemical, molecular, and functional profiles for soil samples were generated by Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, Illumina HiSeq DNA sequencing, and targeted enzyme assays and respiration measurements, respectively. Principal component analysis is a classical way to identify relationships between treatments; it can fail when there is a large number of correlated variables or in the presence of large within-class variability such as in this experiment. Soil FTICR-MS benefited from a feature selection step innovated at PNNL to identify those signature features from within a large set of potentially uninformative variables.

Relevant features were identified through the recursive application of classification trees. This process reduced the number of features from >90,000 chemical formulae with little informative value to 425 key formulae that can be further explored with biological data to reveal the microbial and chemical processes that differentiate the responses of these soils to simulated climate change.

PN13102/2583

Statistical Integration of Omics Data from Microbiomes

Lee Ann McCue

We will develop an infrastructure and computational tools designed to process, analyze, and visualize microbial community sequence data to address the challenge of computational analysis.

Microbes exist and function in communities. Studies of natural environmental or human-associated sites often reveal hundreds to thousands of microbial species co-existing, i.e., a micriobiome. The interactions between microbes within such a microbiome are often complex, as is the impact the microbiome as a whole has on its environment. Deciphering microbial activities in their natural environments is a prerequisite to understanding their functional role in environmental processes. Research efforts to understand the vital roles these communities of microbes play in human health, and environmental sustainability have thus turned to high-throughput technologies to measure the various biomolecules extracted from a sample (its nucleic acids, protein and metabolites) to infer the functional capability and emergent properties of the microbiome.

One of the most readily available data types for microbiome research is nucleic acid sequence data. It is feasible to sequence the DNA extracted from natural microbial communities consisting of many species. However, such DNA samples consist of a composite mixture of the genetic material of all of the community members (i.e., a metagenome), and inferring the functional capability from complex mixtures of genetic material has proven challenging. Further, sequencing technologies are capable of generating approximately a terabyte of data in a week; it requires considerable computing power to process data at this scale.

Our ability to make molecular-scale measurements on microbial systems using high-throughput technologies means that large volumes of data are being generated that require the development of novel analytical tools. Robust analysis of complex data from microbial communities in human hosts and in the environment will be key to understanding their vulnerability to change. Specifically, we tested the accuracy of predicting functional attributes from raw, high-throughput sequence data using hidden Markov models (HMMs) of protein families (functionally related proteins). We used HMM libraries that are broadly available to the scientific community: Pfam, PhyloFacts, TIGRFAM, and FOAM, with sequencing data from the genomic material of well-characterized microbes (Table 1). Based on prior knowledge about these characterized microbes and their complete genomic information, we were able to process the raw sequence data from each microbe and calculate the positive predictive value of our predicted assignments to HMM protein families. For example, a positive predictive value represents that proportion of the predicted functional assignments that are correct. The results in Table 1 show the consistently high positive predictive value of this approach.

Table 1. Positive Predictive Value

Organism	Pfam	TIGRFAM	FOAM	PhyloFacts
Cytophaga hutchinsonii	0.8247	0.8391	0.8275	0.6506
Flavobacterium johnsoniae	0.9182	0.9301	0.5986	0.7244
Shewanella oneidensis	0.8784	0.9092	0.9266	0.8275
Xylanimonas cellulosilytica	0.8838	0.9098	0.9382	0.8340
Aspergillus niger	0.7439	0.7460	0.7703	0.6381
Yarrowia lipolytica	0.8810	0.9035	0.9276	0.7504

Processing the volume of data generated by current sequencing technologies requires access to a compute cluster to handle the typical data volumes. Thus, we developed this HMM protein family analysis approach on the PNNL institutional computing cluster, and we have successfully ported it to a recently purchased PNNL cluster, Constance, and the EMSL computing cluster Cascade. Using these large clusters requires that our method coordinate processing data on hundreds of compute nodes. We accomplished this process by partitioning the data and tasks into subtasks, identifying the data required for subtasks, copying that data to the local disk of individual nodes, processing the data locally, and compiling the results from the hundreds and thousands of subtasks from all the nodes back to a cohesive set of results.

This project has been active for only 6 months, during which time we have focused on testing the accuracy of our approach and its efficiency on high-end computing clusters. Future work will encompass the development of a user-interface and ensuring the availability of this approach to the microbiome research community.

PN15077/2752

Structure and Dynamics of Biological Systems

James E. Evans

The ability to observe "live" biological systems across multiple platforms with various spatial, temporal, and chemical resolutions through this project will provide unique insight for these model systems and validate the versatility of this combined approach.

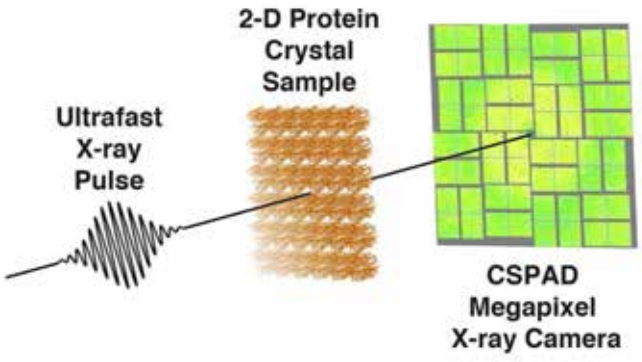
As biological systems are highly complex, understanding how a single protein is related to the function of a whole organism requires spanning more than 10 orders of magnitude across spatial and temporal scales. This is a feat on its own, but a complete picture is possible only if methods are added to probe the chemical and temporal evolution of the system to observe how it changes over time. Biologists have striven since the 1950s to link biological system structures to their physiological function, but countless details remain obscure due to underlying intricacies and wide-ranging processes. Because no single instrument is currently capable of addressing structure, dynamics, and chemistry across all scales simultaneously, new methods integrating data from multiple instruments are required to achieve a clear understanding of biological processes relevant for the production of energy, cleanup of environment, and improvement of human health.

In this project, we are developing, adapting, and employing state-of-the-art approaches toward enabling a better understanding of biofilm organization, enzymatic energy transduction, epithelial cell interactions and organic/inorganic interfaces. We will combine dynamic transmission electron microscopy (DTEM) with femtosecond X-ray diffraction (XRD) at the linac coherent light source (LCLS), secondary ion mass spectrometry (SIMS), and atom probe tomography (APT) to interrogate the structure and dynamics of biological systems.

During FY 2013, significant progress was made with each of our specific project aims. Highlights included acquiring the first transmitted XRD patterns from 2D protein crystals using LCLS, nano-SIMS, and *in situ* time-of-flight (ToF)-SIMS to study biological samples with chemical sensitivity. We developed novel methods for APT to detect the individual protein macromolecules embedded in a resin matrix. Both developments with biological APT and femtosecond XRD of 2D crystals were never before been demonstrated. Additionally, we developed a novel *in situ* liquid cell compatible with femtosecond XRD experiments to image the 2D protein crystals in a fully hydrated state in order to permit pump-probe dynamic observations.

In FY 2014, we continued to develop the multimodal and multiscale platform for interrogating biological systems. In particular, we implemented a more integrated approach by looking at the same sample but using multiple techniques. First, we designed and fabricated new *in situ* liquid cells for X-ray, electron, ion, and optical imaging to allow for a single sample to be transferred between each technique and the correlated images. We also demonstrated novel applications of *in situ* ToF-SIMS and structured illumination microscopy for multimodal imaging of hydrated biological samples, which yielded the first mass spectrometry identification of lipid content in "live" cells.

In FY 2015, we applied the novel *in situ* ToF-SIMS capabilities developed during the previous 2 years toward imaging nanoparticle uptake and nanotoxicity in mammalian cells as well as observed lipid dynamics during biofilm formation. We extended our APT capabilities by designing, building, and implementing an environmental-transfer system that would allow us to run samples in a room temperature state transferred under vacuum or controlled gases or in a cryogenic state. The benefit of transferring samples at low temperature is three-fold. First, the freezing process can be done strategically to prevent the crystallization of water and optimally preserve the sample in its native state thereby avoiding artifacts common to room-temperature biological sample preparation. Second, multiple cryo-compatible instruments for electron and optical imaging already exist onsite and can now be used in conjunction for multimodal imaging. Third, the ability to freeze samples in near-native buffers allows one to tune the local environment and sample conductivity to improve atom probe analysis and interpretation.



Schematic of fixed target diffraction experiments using coherent X-ray diffraction to interrogate protein structure from 2D crystals.

PN13009/2490

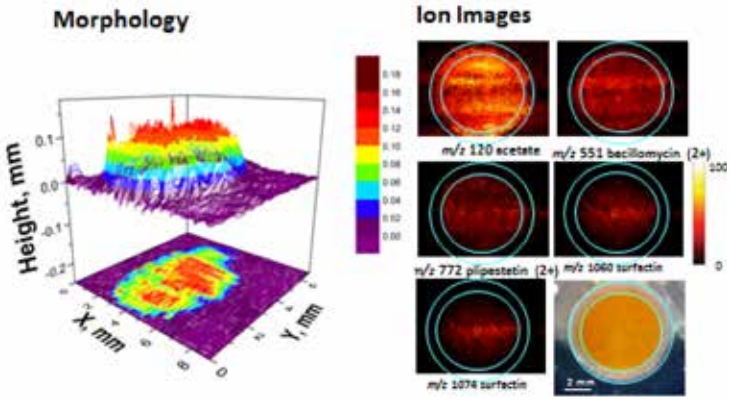
Understanding Cellular Communication and Controlling Directional Flow of Nutrients

Julia Laskin

We are developing unique capabilities for molecular imaging of cellular communication and controlling the directional flow of nutrients and metabolites between cells.

Understanding and controlling intra- and intercellular communication in diverse biological systems is one of the grand challenges in biology. Quantitative imaging of chemical gradients in biological systems with high spatial resolution and high chemical specificity will facilitate understanding cellular communication. This project is focused on developing mass spectrometry imaging (MSI) approaches capable of measuring chemical gradients of individual molecules with 1–10 μm spatial resolution and high chemical specificity. Controlling directional flow of nutrients and metabolites between cells is critical to the rational design of biological systems for a specific function. Combining genetics, molecular biology, high-resolution structural biology, and dynamic imaging yields new methods for controlling cellular response to environmental changes. These responses are examined using the novel nano-spray desorption electrospray ionization (nano-DESI) mass spectrometry imaging capable of mapping chemical gradients of individual molecules released by cells. The combination of these techniques will be used for a detailed understanding of cellular communication in several model systems including well-characterized yeast colonies and plant tissues.

The control of influx and efflux of nutrients, ions, and minerals into plant cells is achieved by designing selective ion transporters. Plants exchange nutrients and metabolites with the environment through their roots formed by single-cell root hairs connected to the larger multi-layer system. The innermost root layer contains the vasculature with xylem and phloem that translocate nutrients and is protected by a single-cell tissue: the endodermis that prevents uncontrolled access to the vasculature. Overall, the system can take high amounts of ions, minerals, and nutrients while excluding potentially toxic substances such as heavy metals.



Simultaneous measurement of morphology (left) and chemical composition (right) of a living 24 hr-old Bascillus subtilis colony on an agar plate.

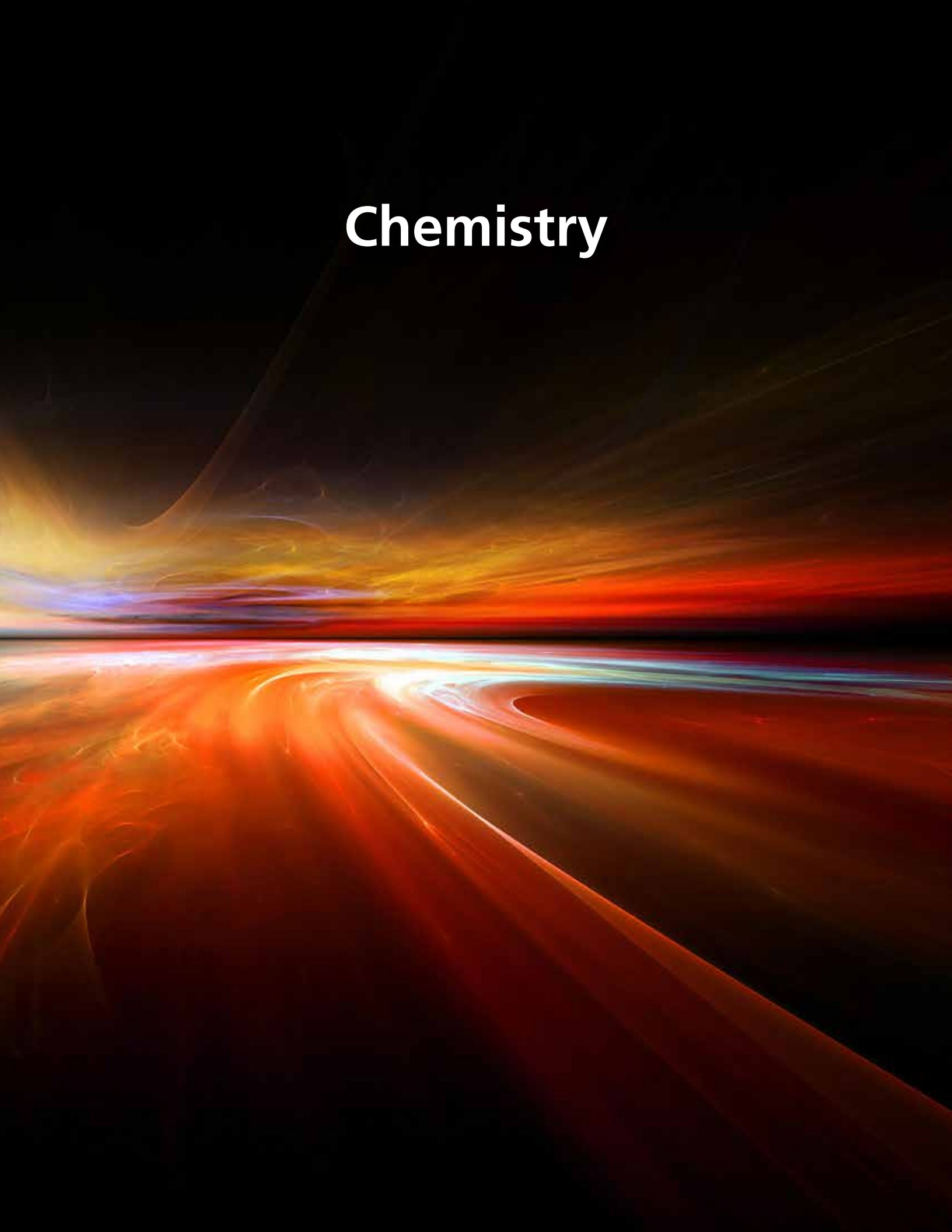
Our focus is on the phytoremediation of strontium by enhancing uptake and storage as insoluble crystals. The only lacking element is a strontium-selective pump localized to the endodermis that will increase strontium uptake from the soil. Ultimately, the implementation of these unique capabilities will position PNNL at the forefront of chemical imaging and will help bridge the mesoscale gap by extending the integrative multimodal imaging platform being developed in the PNNL Mesoscale Pilot project to be applicable to all DOE-BER biological systems of interest from single cells to complex tissues and communities.

In FY 2015, we focused on developing robust tools for imaging of biological samples of arbitrary morphology. We created a unique approach for constant-distance-mode nano-DESI imaging using shear force measurement as a feedback. When the nano-DESI probe approaches a sample, several vibrational modes are affected by the sheer force between components. Using this method, we performed for the first time a simultaneous measurement of the morphology and chemical composition of a living *Bascillus subtilis* colony. The shear force feedback system allowed us to image a 100μ–tall colony while maintaining a constant distance between the nano-DESI probe and colony. The resulting ion images allowed us to identify molecular signatures of both fully and partially developed biofilms. An invention disclosure describing this experimental approach has been submitted, and the results were presented at the annual American Society of Mass Spectrometry Meeting. We also initiated work designing plants capable of removing heavy metals (e.g., strontium) from the environment.

During FY 2016, we will continue the biodesign of plant phytoremediation and use nano-DESI to examine metabolite distribution in the epidermis of these model plants systems. Specifically, we will modify the P2A-ATPase calcium pump and/or an iron transporter already known to be expressed in plant cells to make them selective for strontium and target the epidermis. We will quantify strontium uptake and characterize the modified transporter and its localization in plant tissues using transmission electron microscopy. Subsequently, we will use constant-distance-mode nano-DESI imaging for visualization of metabolite gradients in plant tissues with high spatial resolution and high sensitivity. The results will provide unique insights on the effect of the newly designed protein transporters on the flow of nutrients in the system.

PN15059/2734

Chemistry

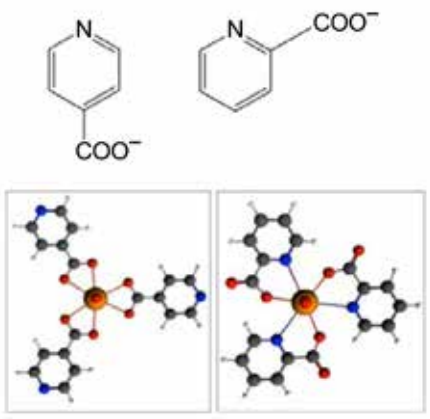


Bio-Inspired Actinides Recognition for Separation Science

Ping Yang

We are developing novel, more efficient strategies for selective separation to allow for better reprocessing of spent nuclear fuels that will reduce the need for long-term waste storage.

Current techniques for the separation of transuranic actinides from lanthanides rely on multi-state liquid-liquid extraction. This approach is challenging from the similar chemical properties of actinides and lanthanides: they are typically present under trivalent oxidation states in acidic solution. A fundamental understanding of the chemical and physical properties of actinide complexes is critical to designing chelating molecular systems rationally and with high selectivity. Nature demonstrates that it is possible to engineer systems with remarkable molecular recognition capabilities among metal ions (e.g., potassium channels show a selectivity factor for K^+ over Na^+ as high as 104:1). The possibility of mimicking such natural design to improve the selectivity to actinides collectively by incorporating multiple binding sites with O, N, and S remains to be explored.



N-donor ligands showing the alpha- and gamma-picoline carboxylate binding to AnO_2^{2+} in different fashions. N,O-coordinated complexes are thermodynamically more favorable than the O,O-bidentate configuration.

In this project, we are observing the physico-chemical interactions of actinides binding motifs and designing chelating reagents with high selectivity to actinides. The research will be based on two main thrusts: the thermo-structural investigation of actinides-bio-ligands complexes and the tuning of redox potentials of actinides compounds through interactions with ligands. We are studying the interactions between actinides and binding sites in select biomolecules using first principle electronic structure methods that include relativistic effects and electron correlation to validate calculations via gas phase collision-induced dissociation experiments and solutions.

In FY 2014, we systemically investigated techniques and uncovered the method that could predict redox potentials for actinide complexes without applying system-specific correction parameters. Further experiments based on free-electron lasers for infrared experiments verified the sulfur-sulfur (S-S) bond structures predicted by theory, the first time that the N,S-coordination chemistry to actinide center was firmly verified in gas phase. Based on FY 2013 results, we further verified differences in binding between uranyl cation and alpha/gamma-picoline carboxylates in solution chemistry.

We focused on a bidentate chelating ligand with hard O- and soft N-donor heterocyclic groups. Alpha and gamma-picoline carboxylate ligands bind to transoxo complexes of An(VI) in different fashions as elucidated by our first-principle calculations using relativistic density functional theory (DFT) methods. We also analyzed and computed binding/dissociative energies, including scalar and spinorbit coupling. The thermodynamically favorable structures of alpha picoline carboxylate actinyl complexes are O- and N-coordinated in preference to bidentate binding with two O atoms. An-N distances were shorter compared with An-O bonds across the actinide series. In contrast, the stable configuration for gamma-picoline carboxylate was bidentate with the carboxylate group in the equatorial plane. Our DFT calculations show that the heterocyclic amine is a strong donor to the actinide center and more favorable compared to the hard O-donor. The results were further verified by gas phase collision induced dissociation (CID) experiments from our Lawrence Berkeley National Laboratory collaborator.

An S-S bond was postulated to reduce actinyl ions during the cellular biological remediation process. Therefore, we chose 2,2'-dithiodipyridine (DTDP), containing one S-S bond that can reduce actinides under mild chemical conditions to study the role of soft S-donor ligands and the redox between actinyl ions and S-S. Relativistic DFT calculations showed strong interactions between actinyl ions and DTDP. We found that both N atoms and one S atom in DTDP coordinate to the actinide center, forming stable tridentate complexes followed by S-S bond activation. Gas-phase CID experiments confirmed the dominant S-S bond cleavage in good agreement with theoretical calculations.

During the first three months in FY 2015, we focused on the manuscript of S-S bond activation. Based on our new conclusion from the redox study that the M06-series provided improved, more reliable redox potentials for actinide compounds, we needed to run all the related calculations with M06 and M06-L functionals. We also performed the calculations using these functionals for the N-donor ligands subproject. At the time of project closure, we were composing two manuscripts for publication based on our project work.

PN13070/2551

Bio-inspired Selective Conversion of Methane to Methanol

Abhijeet J. Karkamkar

To maximize the United States' remote natural gas resources such as off-shore methane, new catalysts are needed to transform methane into liquid fuels such as methanol.

Natural gas can be found in abundance throughout the United States and is often used for heating, cooking, and electrical power generation. Natural gas is composed primarily of methane but is not widely used for transportation. Currently, there are no commercially viable direct approaches to convert methane into liquid fuel, and synthetic approaches are expensive and inefficient at small scales. In this project, we are developing a synthetic pathway to prepare copper cluster of controlled nuclearity. We are also developing catalytic pathways to study the structure of these clusters as they undergo transitions during the catalytic cycle. Our objective is to synthesize and characterize an efficient site for the chemoselective activation of C-H bond in methane and its selective oxidation to methanol (C-OH).The selective oxidation of C-H bond by an oxidant under mild conditions to produce a liquid fuel is a desirable technical accomplishment.

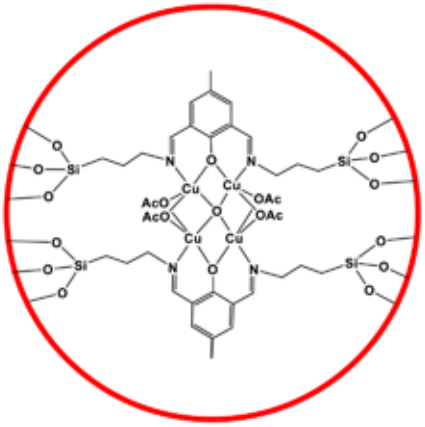
Thermodynamic considerations show that steam reforming (eq. 2) should be favorable only near 1000 K, but that direct oxidation of methane (eq. 1) should be favorable at room temperature. The equilibrium constant for eq. 1 indicates that conversion of 33% at 298 K is achievable. Direct low temperature conversion to methanol will be competitive with steam reforming if it is achieved a single pass conversion of 5.5% with 80% selectivity toward methanol.

$$CH_4 + 0.5\,O_2 \rightarrow CH_3OH$$
$$\Delta Gr_o = -126 \text{ kJ/mol at } 298 \text{ K} \quad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$\Delta Gr_o = +142 \text{ kJ/mol at } 298 \text{ K},$$
$$-27 \text{ kJ/mol at } 1000\text{K} \quad (2)$$

Enzymes such as methane monooxygenase (MMO) are comprised of multinuclear copper clusters that are the proposed active site. There is considerable interest and debate in the literature, however, regarding the exact nature of the active site.

We have designed and synthesized complexes copper clusters with controlled nuclearity. By changing the supported ligand design and metal precursors, we have been able to introduce structural variation in the catalysts. The structure of the ligand and catalysts was characterized by various techniques such as nuclear magnetic resonance, mass spectrometry, and extended X-ray absorption fine structure (EXAFS). These techniques revealed the exact structure of most of these complexes. We also studied the impact of structure of this copper cluster on the catalytic activity for alkane oxidation. To date, we have synthesized and characterized several of the mono-nuclear and multinuclear copper clusters stabilized in a mesoporous organo-functionalized silica matrix and a polyhedral oligomeric silsequioxane (POSS) framework. We are also evaluating the effect of the oxidant on the reactivity and catalytic activity of the oxidation in liquid phase batch and flow reactors.



Structure of tetranuclear oxy-bridged copper cluster supported inside a pure silica MCM-41.

Subtle changes at the metal center have a significant impact on the activity of the catalyst. This finding is of particular importance because we have a very simple method of controlling and tweaking the structure and probing the effect of structure on catalytic activity. We have hypothesized that a trinuclear copper cluster is necessary for oxidation of C-H bond to C-OH. We are now in a position to utilize synthesis as a tool for evaluating catalytic activity in hybrid heterogeneous catalysts.

We have systematically synthesized and characterized and tested a large amount of catalysts. Experimentally for FY 2016, we will select catalytic structures that have shown promising activity and perform detailed kinetic studies and tune the structure to improve yield and selectivity. To this end, we have already identified several two additional mixed metal clusters (iron and copper) that are attractive as catalysts, and we will synthesize and evaluate these potential catalytic materials. Related to this project, one conference presentation (at an American Chemical Society meeting) has been made and one manuscript (in progress as of FY 2015 end) will be submitted within the next year. The skills, publications, presentations, and partnerships resulting from this project are providing the groundwork necessary for attracting future funding.

PN15015/2690

Biomass-Derived Acrylonitrile for Carbon Fiber Production

Michael A. Lilga

This project demonstrates a key catalytic step in the conversion of biomass-derived compounds to acrylates and acrylonitrile, the precursor to carbon fibers used in numerous consumer products.

Developing new pathways for the production of biofuel and bioproducts from lignocellulosic feedstocks is a key objective of DOE's Bioenergy Technologies Office. Products can improve the economics of the refinery. As one example, there has been interest in routes to bio-based acrylonitrile as a precursor to carbon fiber. We have developed novel chemical catalysis pathways to acrylonitrile and acrylates that can be converted to acrylonitrile via known chemistry using ethenolysis.

$$A = B + CH_2 = CH_2 \rightarrow A = CH_2 + B = CH_2$$

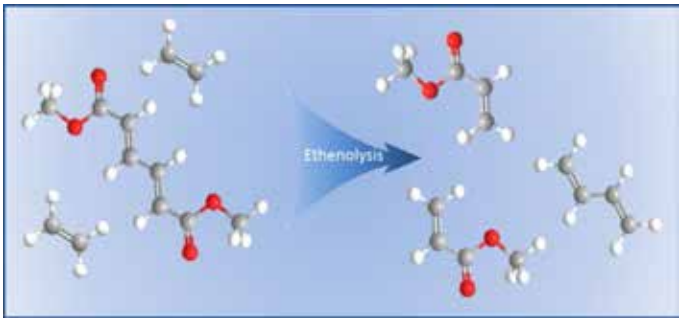
Compounds containing a –CH=CH_2CN or a –CH=CH_2CO_2R (R=H, alkyl) group were studied in proof-of-principle experiments designed to demonstrate feasibility. Successful implementation of this chemistry can improve biorefinery economics and support the production of cost-competitive biofuels and value-added bioproducts.

Several carefully chosen compounds representing a variety of functional groups and structures were tested to determine reactivity with ethylene to form acrylates. Compounds chosen could be obtained from sugars or lignin. The compounds tested included dimethyl fumarate (C4 unsaturated dimethyl ester), fumaronitrile (C4 unsaturated dinitrile), dimethyl muconate (C6 di-eno dimethyl ester), octatrienoic acid (C8 trieno carboxylic acid), and β-angelica lactone (C5 cyclic unsaturated ketone). Reaction temperatures between 40–100°C and ethylene pressures between 14.7–200 psi were used. Owing to their low organic media solubility, dicarboxylic acids were converted to the corresponding methyl esters prior to conducting ethenolysis.

Cat. mol%	C_2H_4 (psi)	Temp(°C)	Conversion (%)	Selectivity to Acrylate	Source of Muconate
5	200	40	54.4	51.1%	Phenol Oxidation
5	200	40	45.8	73.4%	Sigma Aldrich
15	14.7	100	89.5	43.4%	Lignin Oxidation
15	14.7	100	84.9	61.4%	Sigma Aldrich

Yields of acrylate from lignin-derived dimethyl muconate

Results showed that ethenolysis is a promising pathway to the production of acrylonitrile, acrylic acid, and/or methyl acrylate under mild conditions. Fumaro-nitrile gave a 30% yield of acrylonitrile. Interestingly, the carboxylic acid analog dimethyl fumarate provided >5% yield of methyl acrylate. Dimethyl maleate gave a slightly higher yield of ~10%, possibly from higher energy of the cis-carboxylate arrangement. Trans-, trans- (30%) and cis-, cis-(36–54%) isomers of dimethyl muconate both gave good methyl acrylate yields. The cis-, cis- isomer is of interest because it can be obtained from lignin oxidation, offering a potential route to a high value product from this major biomass component. The muconates also produce butadiene, another drop-in chemical product with high value. The octatrienoic acid, which was obtained from sugar fermentation at PNNL, gave <5% acrylic acid because of competitive self-metathesis. The cyclic ketone β-angelica lactone remained unreactive to ethylene; the reverse reaction is more favorable for this substrate.



Ethenolysis of dimethyl muconate to methyl acrylate and butadiene

We successfully demonstrated the production of bio-based acrylates from lignin for the first time. Yields of acrylate from lignin-derived dimethyl muconate provided by Washington State University were comparable to yields obtained from commercial muconate. Overall, our work demonstrated a key step for converting biobased materials obtained from either thermochemical or fermentative routes to acrylonitrile, acrylic acid/methyl acrylate, and other value-added drop-in chemical products. Key findings are that open-chain olefins can be converted using ethenolysis to acrylates and acrylonitrile, cyclic olefinic lactones cannot be converted and reaction conditions are very mild, suggesting low capital upon scale-up.

Outcomes of this project include publication in a peer-reviewed journal, oral and post presentations made at the North American Catalysis Society Conference and the Pacific Coast Catalysis Society Meeting, enhancing PNNL core catalysis capabilities, and proving a novel method to obtain value from lignin that supports the economics of the biorefinery.

PN14008/2592

Climate-Related Chemistry of Internally Mixed Atmospheric Particles

Alexander Laskin

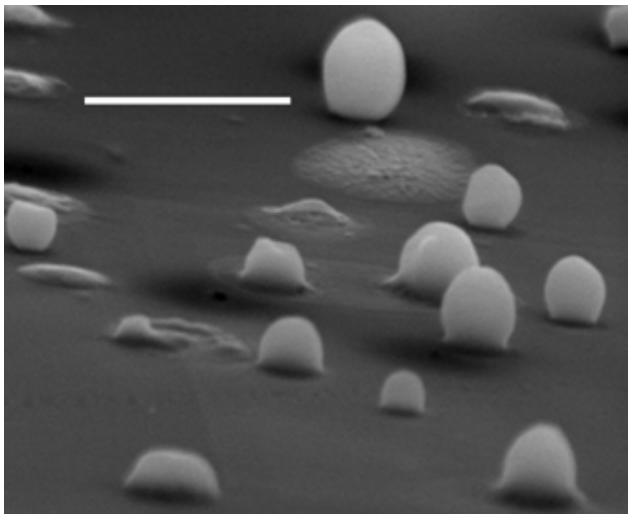
The project applies novel analytical platforms for in depth chemical analysis of atmospheric particles and develops unique capabilities and methodologies for collaborative research in complex particle chemistry and its multi-phase reactivity related to climate change.

Understanding and mitigating the environmental impacts of energy production and use has been identified as one of the important DOE priorities. The production and use of energy often leads to the generation of aerosol particles either through direct emission or through subsequent reactions of gas-phase emissions. For more than a decade, there has been intense interest in studying the role of particles in a broad range of environmental issues, including atmospheric composition and chemistry, assessment of the earth's radiation balance, ozone recovery, and health effects. To address DOE concerns about the safe production and use of energy, it is necessary to develop and apply novel experimental approaches for an improved understanding of the origin and fate of the chemical and physical properties of atmospheric particles.

The intent of this multi-analytical and collaborative research is to characterize the chemical and physical properties of atmospheric particles to establish a quantitative relationship between the composition of aerosols and their atmospheric impact. The ultimate goal is to provide relevant data for use in climate modeling. Our specific research efforts are focused on chemical imaging studies of individual particles and the effects of liquid-liquid and solid-liquid phase separations in internally mixed particles. We will use X-ray spectro-microscopy to investigate particle composition and their propensity for phase separation or phase mixing at atmospherically relevant conditions.

Different occurrences of phase separations depend on particle size, composition, and reactivity of their internal components. These experimental data are of critical importance to elucidate the molecular-level processes governing phase separations in atmospheric particles. The occurrences of phase separations have important implications for particle optical properties, their atmospheric aging, and particle-cloud interactions – the most challenging problems relevant to predictive understanding of aerosol effects on climate change. To this end, we conducted a number of laboratory studies focused on the chemistry of internally mixed organic/inorganic particles and effects of their mixing states on hygroscopic properties, heterogeneous reactivity, and ice nucleation properties. Depending on their composition and ambient conditions, particles exist in liquid, amorphous semi-solid, or solid (glassy) phase states that have important implications in various atmospheric processes.

We showed the first evidence of yet unrecognized atmosphere – land surface interaction resulting in primary generation of submicron airborne soil organic particles (ASOP) composed of solidified dissolved organic matter. Our study suggests that ASOP are efficiently formed after strong rain events in regions where wet soils are exposed to the ambient air. Based on their physicochemical properties, we conclude that ASOP (shown in the figure) is an important aerosol type that may influence the abundance and efficacy of cloud condensation and ice nuclei, absorb solar radiation, and impact the atmospheric environment and carbon cycle at local and regional scales.



Scanning electron microscope images at a 75 degree tilt angle showing abundant appearance of the glassy ASOP in one of the field samples.

We presented a novel method to investigate the mass-based hygroscopicity of aerosol particles while characterizing their spatially resolved elemental and carbon-bonding composition. This method was validated on laboratory-generated aerosols composed of atmospherically relevant salts and sugars. Then, the hygroscopicity and spatially resolved chemistry of complex field-collected atmospheric particles were analyzed that allowed us to infer the hygroscopic behavior of the entire sample.

Obtained data will be used in FY 2016 to begin systematic evaluation of the next generation of cloud models with sufficient fidelity to obtain an accurate model based predictions of environmental and atmospheric processes affected by particles.

PN15065/2740

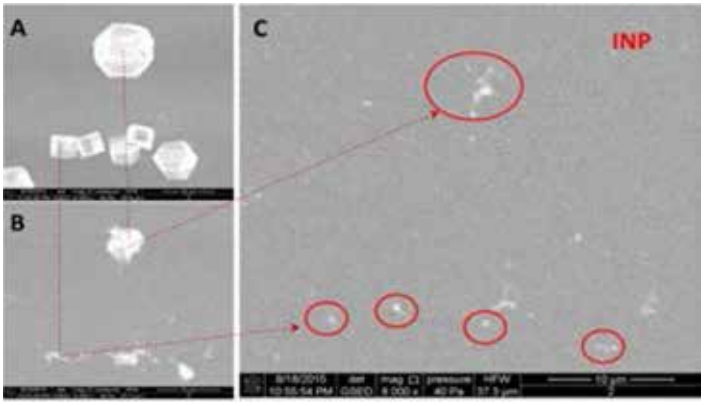
Development of a Novel Microscopy Platform for Fundamental Studies of Ice Nucleation on Atmospheric Particles

Alexander Laskin

The ultimate goal of our project is establishment of a new experimental platform to unravel physicochemical properties of individual INP at microscopic level of detail.

The present understanding of the role that atmospheric particles play in formation of ice clouds is limited to the extent that their impact on the environment and climate cannot be accurately predicted by models. Atmospheric particles are complex in nature (multicomponent and multiphase) and exhibit different ice nucleation efficiencies that need to be probed with individual particle specificity. This project focuses on the development and applications of a novel experimental platform for fundamental studies of ice nucleating particles (INPs) with microscopic determination of physicochemical properties of individual INPs that govern ice formation propensity. The novel platform is hosted by an environmental scanning electron microscope (ESEM) and allows *in situ* experimental studies resembling fundamental processes of aerosol-ice cloud interactions, which are one of the most challenging problems for predictive understanding of the earth's climate change.

The formation of atmospheric ice in clouds can progress by homogeneous and heterogeneous nucleation. For homogeneous nucleation, ice forms when supercooled aqueous droplets freeze. Heterogeneous ice nucleation is initiated by an ice nucleating particle (INP) and can be subdivided into immersion freezing (i.e., ice forms on an INP suspended in a supercooled droplet), deposition nucleation (ice nucleates onto a solid INP surface), and contact nucleation (ice forms in a supercooled droplet when impacted by INP). Our project focuses on heterogeneous ice nucleation, which is governed by the physical and chemical properties of INP that can vary from particle to particle. Previous studies suggested that the following properties may control the efficiency of INPs: insolubility, solid particles such as mineral dust; size, a higher nucleation probability for particle with a larger surface area; chemical bonds and their crystallographic arrangement on particle surface, the ability to form hydrogen bonds; and/or active sites, characteristic locations initiate nucleation such as cleavage and growth steps, crack, cavities, and inclusions. Although these guidelines help to identify which materials are likely to act as INP, they cannot explain the contradicting results observed for real world atmospheric particles, because a microscopic understanding of the ice nucleation events on the INPs is lacking.



IN-ESEM observation of individual ice nucleation events at 205 K and 145% RHice over a sample of field-collected particles: (A) ice crystals; (B) sublimation of ice crystals; and (C) identification of INP (marked with red circles).

In collaboration with Lawrence Berkeley National Laboratory and the State University of New York, our efforts are focused on performing two main tasks. First, we are developing a new capability to allow experimental observation of ice nucleation (IN) inside an ESEM instrument over individual INPs at temperatures (T) as low as 180 K and relative humidity (RH_{ice}) typical for the upper troposphere/lower stratosphere. Our second task is the application of the IN-ESEM platform to investigate ice nucleation of complex atmospheric particles relevant to anthropogenic and biogenic emissions. Combined with theoretical chemistry calculations, the experimental data will be analyzed to gain a better understanding of INPs and parameterizations for cloud models.

We designed, fabricated, and constructed the cryogenically cooled ice nucleation cell, which is a core part of the IN-ESEM platform. We achieved precise temperature and RHice control over the sample, confirmed by the comprehensive set of measurements conducted

PN14066/2650

over INPs (kaolinite particles) with known IN efficiencies. Next, a comprehensive set of experiments was conducted to evaluate the performance of the platform and demonstrate its applicability for systematic studies of ice nucleation over a broad range of temperatures relevant to formation of atmospheric ice (200–260K). Presently, we use this platform to study ice nucleation propensities of INPs generated in laboratory experiments and ambient particles collected in field studies. The figure illustrates the identification of INPs in our IN-ESEM experiment, within which the locations (x–y coordinates) of INPs are precisely recorded, followed by an in-depth analysis of INP composition and structures.

At the next stage of the project, we will utilize this platform in systematic studies and focus on predictively understanding the fundamental relationship between particles ice nucleation propensities and their chemical composition. Spectromicroscopy analyses of individual INPs will assess the chemical composition, inclusions, and surface features that are efficient to induce the formation of ice. Complementary theoretical chemistry modeling of selected systems will be used to understand further the experimental results and relate them to fundamental macroscopic and molecular level properties of INPs.

Dynamics of Supported Noble Metal Nanoparticles in the Presence of Oxidizing Environment: Application of Compressive Sensing in ETEM

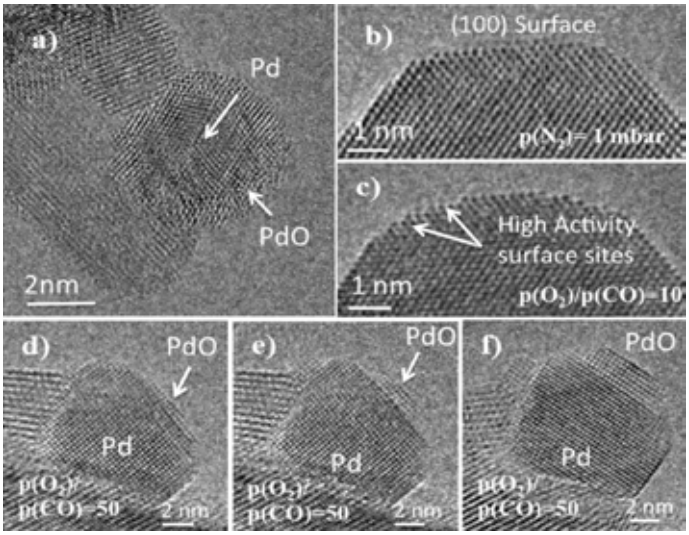
Libor Kovarik

The goal of this project is to investigate the dynamic behavior of catalytic nanoparticles during exposure to elevated temperature and reactive environment to establish a structure property relationship and develop design principles for accelerated discovery of next-generation catalytic materials.

Supported metal nanoparticles are extensively used in catalytic applications under a high temperature reactive gas environment in which the environmental setting can lead to a range of morphological, structural, and surface transformations. Understanding these transformations is critical for explaining functional properties and is a key requirement for developing successful design principles. The objective of this project is to study the dynamics of the surface and structures transformation of platinum group catalytic nanoparticles during CO oxidation and other catalytically relevant environmental conditions.

To achieve this goal, we applied and further developed the state-of-the-art aberration corrected environmental transmission electron microscopy (ETEM) capabilities for atomic-resolution imaging under dynamic operating conditions. ETEM provides a unique capability for analyzing morphological and structural transformations at atomic scale. However, it has restrictions for studying the broad range of material's transformations due to the limitations associated with temporal resolution and electron-dose effects. As part of this project, we worked toward establishing the compressive sensing capability for ETEM, which is expected to improve temporal resolution or correspondingly reduce the electron dose by an order of magnitude. The work was performed in collaboration with Direct Electron, LP and involved designing and building a compressive sensing video acquisition camera. As this capability was still under development in FY 2015, the majority of the experiments from the previous year were performed with conventional CCD and a direct detection camera that was installed on ETEM under a loan contract. Direct detection cameras offer high sensitivity and enable an order of magnitude higher readout rates, a critical feature for studying the dynamics of catalytic nanoparticles.

The main portion of our research effort in FY 2015 focused on studying the dynamic behavior of Pd nanoparticles during CO oxidation, which often displays complex oscillatory behavior and has been associated with dynamic structural changes. However, the nature of these changes remains to be established; it has been hypothesized that PdO oxide reformation is responsible for the oscillatory catalytic behavior. To understand this phenomena, we studied Pd nanoparticles catalysts under controlled gas conditions of $p(O_2)/p(CO)$ in the 200–300°C temperature range. In the absence of CO, it was determined that the environmental exposures led to the formation of a PdO oxide shell that shares epitaxial relations with Pd and is highly distorted. The mechanism of PdO shell formation was established at the atomic level, and the imaging enabled us to describe previously unknown process of nucleation and growth.



The dynamics of Pd nanoparticles during CO oxidation conditions: a) Pd/PdO transformation during exposure to oxidizing environment; b,c) a dynamic restructuring of Pd surfaces during CO oxidation; and d,e,f) the formation of PdO during CO oxidation.

PN15055/2730

Under lean CO oxidation condition, PdO formation has been found to be greatly inhibited, and it was determined to follow a distinct transformation path. Additionally, PdO forms on specific facets, and the overall formation can reverse in the initial stage of the CO reactions, indicating high CO conversion. However, steady state oscillations of the oxide species have not been established. Under higher p(CO) conditions, it was determined that Pd surfaces remain metallic and can be highly dynamic. Significant activity has been observed on low index surfaces (100), which undergo significant restructuring and display high activity of surface atom movements, suggesting the presence of active sites.

In addition to studying the dynamic PdO formation during CO oxidation, we also addressed the mechanism of PdO reduction and the role of particle support on the mechanism of transformation. During a collaboration with a group from the Georgia Institute of Technology, we studied the effect of preparation methods on the performance of Co/Al_2O_3 catalysts for dry reforming of methane. Overall, the work of this project has enabled us to gain a new level of understanding metal-supported catalysts. Thus far, our work has led to four presentations (three of which were invited) and publications in three peer reviewed journals: *Chemistry of Materials, Journal of Materials Science*, and *Journal of Physical Chemistry C*. As of the end of FY 2015, an additional publication is in preparation for submittal. During FY 2016, we will be identifying the factors that dictate the kinetics of oxide transformation for Pd nanoparticles supported on various oxide types.

Electrocatalytic Reduction of Phenols and Ethers

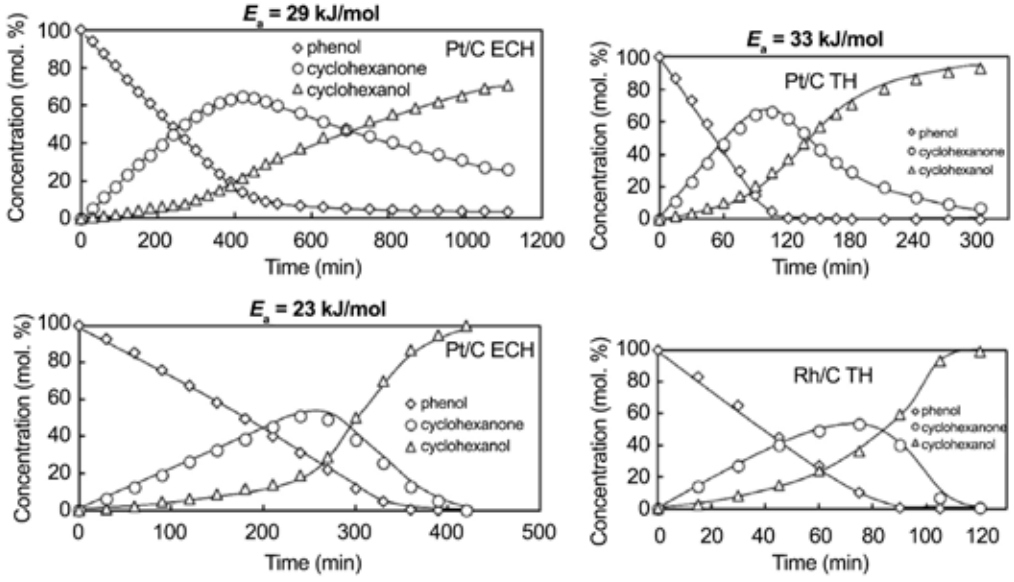
Donald M. Camaioni

In this project, we are examining the pathways and challenges of catalyzing low temperature electrochemical processes for electrical energy storage in the form of hydrogen carbons suitable for transportation fuels derived from the lignin components of biomass.

Biomass is the oldest renewable energy supply; however, many biomass and bio-oil feedstocks are not used for modern transportation due to high levels of oxygenation. A wealth of catalysis research exists to convert aqueous bio-oils thermally into hydrodeoxygenated liquid hydrocarbons through reaction with hydrogen. However, for locations where high temperatures and high pressure hydrogen are not available, the best route to convert biomass groups to hydrocarbons is unclear. Previous work has shown that model biomass compounds such as phenol can be electrochemically converted to products such as cyclohexanone, cyclohexanol, and cyclohexane using metal electrocatalysts.

Our project focuses on understanding how a system operates to produce on-demand fuels from bio-oil, along with the catalysis limitations on such a process. It consists of evaluating thermal and electrocatalytic reduction of phenol, substituted phenols, and aryl ethers in aqueous systems using carbon supported metal catalysts. From this work, we hope to improve understanding of the mechanism, rate-limiting steps, and energies required for the electrocatalytic reduction and compare these findings to traditional thermal hydrogenation. Our research will evaluate a process to produce transportation fuels sustainably and securely using renewable feedstocks at a wide scale of plant sizes, even in decentralized locations. A challenge for the future will be how to provide energy reliably in the face of both climate change and vanishing natural resources. It is anticipated that our work will contribute to energy security by developing processes for producing liquid hydrocarbon transportation fuels on demand at any location in a renewable manner without greenhouse gas emissions and also absent the risks associated with using a depleting fossil fuel source with extremely volatile availability.

In the past year, electrocatalytic and thermal reactor systems to test for biomass hydrogenation were designed and set up. The necessary analytical tools to evaluate conversion and selectivity were developed and optimized to maximize the accuracy of measured reaction kinetics. The metal surface area (dispersion) of several carbon-supported metal catalysts was determined using hydrogen chemisorption and electrochemical methods, and particle size was measured using electron microscopy. By measuring the rates of phenol conversion to cyclohexanone and cyclohexanol using gas chromatography and normalizing to the number of available sites, the electrolyte that resulted in the highest rates was determined to be acetic acid at pH 5. Of three catalysts evaluated (Pt/C, Rh/C, and Pd/C), Rh/C had the highest rate



Concentration profiles of phenol and the products (cyclohexanone and cyclohexanol) of electrocatalytic (ECH) and thermal hydrogenation (TH) on Pt/C and Rh/C. Reactions performed at room temperature in acetic acid at pH 5; ECH conducted at –40 mA; TH conducted with an atmosphere of hydrogen. Arrhenius activation barriers shown above the plots were determined from the initial rates of phenol conversion measured from 5–40°C.

PN15099/2774

(2–3 times more activity than Pt/C, much higher than Pd/C). Activation barriers for Pt/C were measured for both the electrocatalytic and thermal hydrogenation of phenol over a temperature range of 5–40°C and found to be similar (~30 kJ/mole), indicating a similar rate-controlling step. The reaction order in phenol was determined to be zero-order for Pt/C and Rh/C.

The most important finding during FY 2015 was that the mechanism for the electrocatalytic hydrogenation of phenol on platinum group metals appears to be the same as the thermal hydrogenation, and much of what is understood about the mechanism at higher temperatures (200°C) extends to the low temperatures investigated here. The only major difference between electrocatalytic (ECH) and thermal hydrogenation (TH) observed thus far is the origin of the hydrogen reduction equivalents (hydrogen or water). The similarities between ECH and TH allow theoretical models to of the mechanism and solvent effects for TH to be extended to ECH. The major differences between ECH and TH are expected to be hydrogen coverage on the catalyst surface, which is controlled by hydrogen pressure in the thermal process and by the electrochemical potential in the electrocatalytic process.

Next year, we plan to investigate further the phenol hydrogenation process and extend to other substrates, including aryl ethers, which more closely resemble the lignin-derived structures commonly found in bio-oils. The boundaries of electrocatalytic hydrogenation of phenol and aryl ethers will be tested. Because the maximum temperature and ideal current density for ambient pressure electrocatalytic hydrogenation of phenol are unknown, we will explore the effects of increasing temperature and current density on rates of phenol conversion and on product selectivity. We will also develop kinetic models to explain the higher activity on Rh/C compared to Pt/C. The adsorption energies of reactants on the different metal catalysts may help us understand the difference in activity; therefore, we will attempt to measure such energies using solution calorimetry.

Fundamental Understanding of Nucleation Processes to Assess Solution Stability and Phase Growth and Genesis

Gregg J. Lumetta

We are developing a physicochemical framework for predicting and manipulating precipitation reactions relevant to nuclear materials processing and nuclear forensics.

Nucleation and crystal growth are fundamentally important to processing nuclear materials and radioactive wastes, but investigation of the basic science underlying nucleation in relevant systems is lacking. Understanding these phenomena is important because they underlie certain aspects of nuclear forensics. Specifically, the successful processing of legacy nuclear wastes requires the control of solids precipitation, and many chemical processes used in the nuclear industry involve highly concentrated salt solutions. Precipitation of solids from such solutions, however, is often a concern. In this context, precipitation might be desired (e.g., of plutonium oxalate during plutonium oxide production) or not (e.g., during ion exchange or solvent extraction processes).

Under this project, we are developing a framework based on recent developments in crystal growth that have been providing insight into two distinct approaches. In the "classical" pathway, nucleation occurs through ion-by-ion addition to a growing cluster with increasing free energy of formation until a critical size is reached. At this point, the free energy change for further growth becomes negative and occurs via ion-by-ion addition to kink sites at atomic steps on the crystal surface. For both nucleation and growth, morphologies and dependencies of rates on applied supersaturation are well understood and are distinct from those of crystals that form through the second "non-classical" pathway. In this scenario, nucleation and growth occur through the addition of higher order species ranging from oligomeric complexes to liquid droplets to amorphous or crystalline nanometer-scale particles. Detailing the morphologies, internal structures, and dependencies of growth rates on supersaturation allows the formation mechanism to be determined and related to process conditions. Moreover, rate measurements vs. supersaturation and temperature will allow us to determine the activation barriers that control the nucleation and growth processes.

Our research is focused on the precipitation of oxalate salts. In particular, we are investigating nucleation and crystal growth of Pu(III) oxalate, $Pu_2(C_2O_4)_3 \cdot 10H_2O$, because the way this compound forms is of interest to the nuclear forensics community. From the challenges of working with the highly radiotoxic plutonium, initial investigations have used Ce(III) and Eu(III) as surrogates for Pu(III), which will allow the development of the experimental techniques to examine the plutonium system safely. Investigations into the precipitation of sodium oxalate from high-salt alkaline solutions will also be pursued because this system is critically important to operation of the Hanford Tank Waste Treatment and Immobilization Plant.

A combination of theoretical and experimental techniques is being used to develop a framework for explaining nucleation and the subsequent crystal growth of the metal oxalate systems from the atomistic to hundreds of micrometers scale. Both classical and *ab initio* molecular dynamics (MD) simulations will be performed to provide direct but complementary information on the mechanisms underlying phase transformations. Experimentally, these systems will be investigated using advanced *in situ* electron microscopy techniques to gain insight into the nucleation mechanisms involved. This work will use techniques previously demonstrated through *in situ* transmission electron microscopy (TEM) investigations of $CaCO_3$, gold nanoparticles, and iron oxide nanoparticles. In addition, cryo-TEM will be used to provide "snapshots" of particle growth with minimal disturbance to the system. Other techniques will be used to guide the conditions chosen for the microscopy studies and to provide additional insight into metal oxalate crystal growth, including optical spectroscopic techniques and high-resolution ultrasonic spectroscopy.

PN15085/2760

As entry into the MD simulations, it is initially necessary to benchmark quantum mechanical gas phase complexes and the spectral signatures of their corresponding solvated species to build a foundation for larger-scale frameworks. These fundamental steps will aid in developing classical interaction potentials for larger molecular dynamics simulations of the supersaturated solutions. To this end, the electronic ground state for the Pu^{3+} ion was calculated and found to be $^6H_{5/2}$, consistent with the experimental value reported in the literature. Based on this information, the interaction energetics of Pu^{3+} with water as {$[Pu(H_2O)]^{3+}$ and $[Pu(H_2O)_9]^{3+}$} and with oxalate as{$[Pu(C_2O_4)]^+$ and $[Pu(C_2O_4)_3(H_2O)_3]^{3-}$} were calculated. The value of –5.0 eV obtained for $[Pu(H_2O)]^{3+}$ agrees well with the experimental value of –4.6 or –4.1 eV (depending on a coordination number of 8 or 9), especially given the fact that the zero-point-energy has been neglected.

A major challenge of investigating precipitation phenomena by *in situ* microscopy is choosing the solution conditions in which the precipitation does not occur too fast (in which case the precipitation event would be missed) yet is fast enough to be observed within a reasonable time frame. To help define such conditions for the Pu(III) oxalate system, optical spectroscopy methods are being used to monitor the precipitation of the analogous Eu(III) oxalate species from HNO_3 media.

Complexation reactions of Eu(III) can be conveniently monitored by luminescence spectroscopy. The hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition at ~615 nm is very sensitive to the coordination environment around the Eu^{3+} ion and increases dramatically in intensity relative to the $^5D_0 \rightarrow {}^7F_1$ transition at ~592 nm, at which point the oxalate displaces water from the primary Eu^{3+} coordination sphere. Thus, monitoring the intensity ratio of these two spectral bands in the luminescence spectrum over time provides a means to determine the relative rate of the Eu(III) oxalate formation.

A similar methodology can be employed using Fourier transform infrared (FTIR) spectroscopy with an attenuated total reflectance (ATR) cell. For example, $Eu(NO_3)_3$ (40 mmol/L) and $H_2C_2O_4$ (7.5 mmol/L) were mixed together in 0.5 mol/L HNO_3. The solution was placed on a diamond ATR cell, and the FTIR spectra were recorded at ~1-min time intervals. The formation of Eu(III) oxalate was indicated by appearance of (and subsequent increases in) the bands at 1317, 1362, and 1602 cm^{-1}. This type of experiment can be used to determine relative rates of precipitation of trivalent f-block metal oxalates and to identify candidate conditions rapidly for the *in situ* microscopic examination of these systems.

Different morphologies are obtained when trivalent f-block metal oxalates are produced under slightly varying conditions. The optical micrographs of Eu(III) oxalate show distinctly different patterns depending on the Eu-to-oxalate ratio and initial mixing temperature. A Pu(III) oxalate crystal grown by a hydrothermal synthetic technique resembles the Eu(III) oxalate species grown by mixing Eu nitrate and $H_2C_2O_4$ solutions at 80°C. These findings verify that Eu(III) is a reasonable surrogate for Pu(III) in developing our experimental techniques.

In FY 2016, work will continue on developing the theoretical framework for MD modeling of Pu(III) oxalate nucleation. The approach will include calculating the electronic and vibrational spectra of the hydrated Pu(III) cation and its oxalate complexes and developing the interaction potentials for large-scale simulation of crystallization. *In situ* microscopy and cryo-TEM methods coupled with optical and high resolution ultrasonic techniques will be used to determine the mechanisms and pathways to nucleation of f-element oxalates and relate these to the morphology of the resulting solids. A key emphasis of our work in the next year will be the transition to using these techniques with Pu.

Localized Surface Plasmon Resonance Spectroscopy, Microscopy, and Sensing

Patrick Z. El-Khoury

This project combines nanoscopic (chiefly, surface- and tip-enhanced Raman) and theoretical (static and dynamic quantum chemical simulations) tools to probe the interplay between a single molecule and its local environment.

Efforts to reach the ultimate detection limit (i.e., the sensitivity required to probe 1.66 yoctomoles [$1/N_A$]) of a substance-rendered the art and science of engineering plasmonic nanojunctions popular over the past few years. This is a consequence of the extreme localization of electromagnetic fields between plasmonic nanostructures, whereby the detection of the feeble optical response of a single scatterer is feasible. The effect is most evident in surface- and tip-enhanced Raman scattering (SERS and TERS) from molecules coaxed into plasmonic junctions. Through this project, a combination of experiment and theory is aimed at understanding the operative mechanisms that govern optical spectroscopy at plasmonic nanojunctions. The acquired knowledge is then used to rationally design and fabricate ultrasensitive plasmonic sensors.

Our FY 2013 work revealed that inelastic photon scattering at plasmonic junctions retrieves molecular polarizabilities and broadcasts intimate details about the environments in which the molecular scatterers reside as well as interplay between molecules and plasmons. We employed density functional theory (DFT) tools to compute the Raman spectra of 1,3-propanedithiol (PDT) molecules in various media. In FY 2014, we combined atomic force microscopy (AFM)-based TERS point spectroscopy, within which the AFM is operated in non-contact mode with the single-molecule framework developed in FY 2013. We recorded sequences of Raman spectra at a plasmonic junction formed by a gold AFM tip in contact with a silver surface coated with 4,4'-dimercaptostilbene (DMS). Our findings were rationalized with the charge-transfer theory of Raman scattering and DFT calculations, illustrating how current carrying plasmons modulate the vibronic coupling terms from which intensities of the bu states are derived. In effect, we identified gateway molecular modes for mediating charge shuttling across a plasmonic gap.

In FY 2015, we further developed our TERS nanoscale chemical imaging capability and performed multi-modal imaging of novel plasmonic substrates using the suite of cutting-edge microscopy tools housed within EMSL at PNNL. Four key articles were published in *The Journal of Physical Chemistry C, The Journal of Chemical Physics, Faraday Discussions*, and *Nano Letters*. Non-resonant TERS images of DMS molecules adsorbed on silver revealed that different vibrational resonances of the molecules are optimally enhanced at different sites of the metal surface. These results can be understood on the basis of our prior years' results and analyses; specifically, nanoscale TERS chemical images that map interaction between vibrational mode-dependent polarizability tensors of DMS and enhanced electromagnetic fields at a plasmonic tip-surface nanojunction. Recorded TERS chemical images provided insights into specific molecule-metal interactions. By virtue of the molecular reporter symmetry used, we demonstrated how non-totally symmetric vibrational modes of DMS (bu modes) map differences in vibronic coupling strength across a metal surface. Overall, we found that each pixel in recorded TERS images potentially can be used to broadcast intimate details about the local environments in which molecules reside.

Also in FY 2015, we investigated plasmonic properties of a self-assembled 2D array of Ag nanospheres. The structures of individual particles and their assemblies were characterized using transmission electron microscopy. The plasmonic response of the nanoparticle network was probed using two-photon photoemission electron microscopy (TP-PEEM), which revealed the structure and plasmonic response of the plasmonic nanoparticle network to be homogeneous. A notable agreement between experiment and theory allowed us to account rigorously for the observable vibrational states of biphenyl-4,4'-dithiol (BPDT) in the ~200–2200 cm^{-1} region of the spectrum. Finite difference time domain simulations further revealed that physical enhancement factors of 106 are attainable at the nanogaps formed between the silver nanospheres in the 2D array. Combined with modest chemical enhancement factors, this information enabled reproducible single-molecule signals from the easily self-assembled SERS substrate.

PN13092/2573

We used the same substrate for single-molecule SERS spectroscopy, describing experiments in which molecular coverage was systematically varied from 3.8×10^5 to 3.8×10^2 to 0.38 molecules/μm^2 using electrospray deposition (ESD) of ethanolic DMS solutions. Compared to their ensemble averaged analogues, spatially and temporally averaged spectra of single molecules exhibited several unique features, including distinct relative intensities of the observable Raman-active vibrational states, more pronounced SERS backgrounds, and broader Raman lines indicative of faster vibrational dephasing. Using our single-molecule framework, we derived a unique molecular orientation in which a single DMS molecule was isolated at a nanojunction formed between two silver nanospheres in the 2D array.

We assigned the broadened spectra along the SERS time sequence – which sum to a SERS background in the averaged spectra – to instances in which the π-framework of the DMS molecule is parallel to the metal at a classical plasmonic nanojunction. This result also accounted for the observed Raman line broadening as a result of fast vibrational dephasing and driven by molecular reorientation at a plasmonic nanojunction. Notably, we found that in the case of a single DMS molecule isolated at that nanojunction, molecular orientation may affect the derived single-molecule SERS enhancement factor by up to five orders of magnitude. Accounting for chemical effects and molecular orientation, we estimated a single-molecule enhancement factor of $\sim 10^{10}$ in our measurements.

Finally, we reported tip-enhanced Raman imaging experiments in which information on sample topography and local electric fields was simultaneously obtained using our all-optical detection scheme. We demonstrated how a Raman-active DMS-coated gold tip of an atomic force microscope can be used to simultaneously map the topography and image the electric fields localized at nanometric slits lithographically etched in silver. Bi-modal imaging was feasible by virtue of the frequency-resolved optical response of the functionalized metal probe. Namely, the probe position-dependent signals could be sub-divided into two components: a 500-2250 cm^{-1} Raman-shifted signal and a sub-500 cm^{-1} signals arising from mirror-like reflections of the incident laser field off the gold tip. Using these molecular signals, we demonstrated that sub-15 nm spatial resolution is attainable using a 30 nm DMS-coated gold tip. We also showed that the reflected low-wavenumber signals trace local electric fields in the vicinity of the nanometric slits.

In FY 2016, we will continue to seek the rational design of plasmonic sensors based on the results realized thus far.

Making, Measuring, and Modeling Materials for Quantum Computing

Nathan A. Baker

The goal of this project is develop a basic science understanding of quantum computing materials and the tools and techniques that can be applied to many of the most promising qubit architectures.

Materials science has a well-established approach for the design of new materials and improvement of existing materials represented as the "make, measure, model" mnemonic.

Make. To make, the existing PNNL materials synthesis capabilities demonstrate the preparation of quantum computing (QC) materials by preparing nanostructured QC materials through focused-ion beam methods; improving the fabrication of QC devices through post-processing to remove photoresist residue from delicate device features.

Measure. Existing PNNL chemical imaging capabilities will demonstrate the characterization of QC materials by developing novel sample preparation methods that enable analysis of unique and delicate structures for materials of interest to the QC field; developing new methods in z-contrast scanning transmission electron microscopy (STEM) to characterize structures of interest to QC; and using atom-probe tomography (APT) to understand the structure and chemical composition QC structures.

Model. Existing PNNL mesoscale materials modeling and mathematics capabilities will be developed in the simulation of QC materials by evaluating the impact of materials defects on the performance of topological QC paradigms.

From this broad continuum of technical focus areas, PNNL will develop not only a basic science understanding of the QC materials but also the tools and techniques that can be applied to many of the most promising qubit architectures (i.e., quantum dots, defects in solids, and superconducting Josephson junctions).

The task of developing a supercritical fluid-based wafer cleaning capability was divided into two parts. The first was to design, build, and test a modular supercritical fluid system that could be easily adapted to suit different cleaning procedures. The other part of this effort was to establish a cleanroom capability that would provide a means of patterning, etching, and depositing aluminum features on silicon wafers. Samples could then be generated with a hard-baked photoresist in different ways and used to gauge the performance of the new cleaning system.

A high pressure system capable of generating conditions needed for supercritical fluid media was successfully built with a dual-line configuration of syringe pump, mixing vessel, and cleaning chamber. This parallel construction affords the ability to operate at two different pressures simultaneously. Samples could be soaked at lower pressure ranges and sprayed with higher pressures of supercritical fluid. The mixing vessels in line with both manifolds provided an effective dissolution of stripping agents in the supercritical fluids and acted as reservoirs for either filling or spraying fluid into the cleaning chamber. Digital readouts for pressure and temperature were installed across the system so that precise cleaning conditions could be logged over time for later replication with a commercially available system. Protocols for spin-coating and UV exposure of I-line resist were developed and tested for use with the evaporative deposition of micron-sized aluminum features. Masks that provided thin, interdigitated structures were chosen as a model template for cleaning studies. The closely connected features hindered subsequent lift-off and were found to contain residual resist, which are ideally suited for cleaning studies. These wafer samples are being actively used to evaluate and improve the performance of the supercritical fluid cleaning system for work in FY 2016.

For the measure aspect of the project, the majority of research transitioned to an externally funded follow-on project. The modeling research specifically focused on topological phases of matter, how defects affect these phases, and how these phases relate to quantum measurement and computing. Much of this work is ongoing and will be the focus of FY 2016 efforts.

Our team worked to develop new bounds for the Egyptian fraction problem with few prime factors, an important mathematical problem dating back thousands of years with applications in electrical engineering, geometry, and topological phases of matter. The previous best known bounds were exponential, whereas ours are linear. This dramatic improvement should allow us to classify integral modular categories

PN15080/2755

through rank 15, of broad interest to the mathematical community and vital to the study of topological quantum computation. Additionally, it is a necessary step for understanding how the disorder affects topological phases. This work will enable new studies related to disorder and computational power in FY 2016.

A collaboration was initiated to understand the effects of non-standard lattices in models for topological quantum computing. Preliminary studies showed that these non-standard lattices can improve the robustness of the system in the presence of noise and defects. It is believed that the lattices may also have implications in wave guides and meta-materials. We have also begun to investigate how the mathematics used to study topological phases of matter applies to nucleotide pseudo-knots. This work is ongoing and promises to have implications in DNA origami, nucleotide conformation, and the behavior of amino acid chains in thermal environments. The team has worked with external researchers to understand how fermions can be incorporated into certain models for topological phases of matter.

Additional team members have explored the implications of new combinatorial approaches to optimal quantum measurements. There has been investigating into the relationship between symmetric informationally complete positive operator valued measures, mutually unbiased bases, and mutually unbiased subspaces. Combinatorial techniques have been brought to a classical algebraic/geometric problem. Another collaboration was formed to understand the algebraic building blocks of topological phases of matter that succeeded in understanding the algebraic properties of loop braid groups that have applications in (3 + 1)-dimensional topological quantum field theory, classifying all topological phases of matter that have five particle species, classifying topological phases to understand how they behave in the presence of disorder, and showing that there are only finitely many premodular categories of fixed rank. In ongoing work, we are continuing to study classes of categories that describe gauged symmetry (and disorder) and how one can incorporate fermions back into a bosonized quantum field theory.

The above work has resulted in five papers currently under review, six papers in preparation and contingent on ongoing research, a special session at the Joint Mathematics Meetings, an accepted proposal for a special session at the 2016 AMS Spring Western Sectional Meeting, three new hires, and four conference/workshop invitations.

Marine Radiochemistry: First Th-231 Measurements in Seawater for Tracing Rapid Particle Dynamics

Jon M. Schwantes

In this project, we are understanding and controlling radiochemical separations as key to characterizing current nuclear materials and processes and developing the next generation of nuclear characterization technologies.

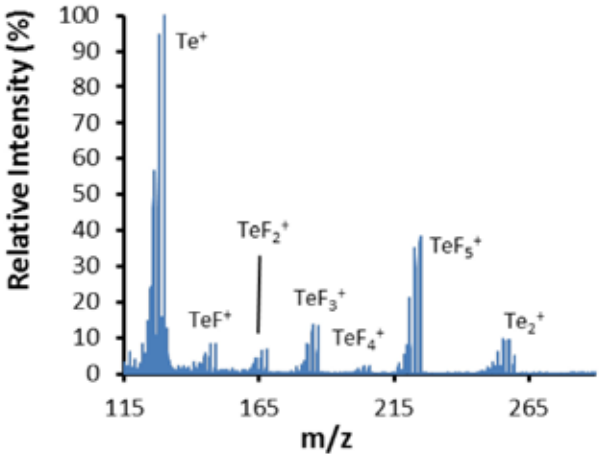
The primary goal of this project is to develop advanced capabilities in radiochemical separations both during fuel irradiation for sequestration purposes and after environmental dispersal for monitoring and remediation. Continued advancement of these separation and measurement techniques is critical to maintaining state-of-the-art capabilities in the collection and detection of radioactive materials. Our efforts are divided into three tasks that are detailed below.

Marine detection of ^{231}Th. Suspended particles are a large carrier of radionuclides in oceanic systems. Uranium and thorium display unique interactions with particles in ocean environments with uranium remaining dissolved as a carbonate complex and thorium adsorbing to any available particle. This behavior allows uranium/thorium parent/daughter ratios to be useful for tracking particle and colloid movement in the ocean by establishing the deviations from secular equilibrium as their loss within the water column due to agglomeration, flocculation, and settling. However, this ability is limited by the time that is necessary to establish secular equilibrium between the parent and daughter. Processes can be developed occurring at rates much faster or much slower than the time to reach secular equilibrium are not observable.

The ^{238}U/^{234}Th ($t_{1/2}$ = 24.1 d) ratio has been widely used for tracking particulates on relatively long time scales. Our project efforts are extending these capabilities by performing the first measurements of ^{231}Th, daughter of ^{235}U, in seawater for tracing rapid particle motions. Although the brief half-life of 25.5 h for ^{231}Th is extremely desirable for such measurements, the small abundance and rapid decay of the isotope has prevented its use as a tracer in the past.

During the first year of this effort, we evaluated various techniques for separating thorium from seawater and selected a method based on the co-precipitation of thorium with MnO_2, followed by filtration and washing to remove other species. In addition, measurement techniques that would be suitable to both an *in situ* measurement and rapid data collection needed to assess timing data for ^{231}Th were evaluated. In FY 2015, we succeeded in constructing a detector system capable of performing beta-gamma coincidence detection on ^{231}Th and collected spectra from the pure isotope milked from a ^{235}U parent solution and ^{231}Th precipitated with MnO_2 from artificial seawater spiked with a solution leached from natural uranium ore. Precipitations with real seawater at full scale have been prepared, and results were to be available at the beginning of FY 2016.

Development of NF_3 mass spectrometry. Traditional extraction of actinides from environmental samples for mass spectrometry can involve multiple radiochemical separations and require considerable time, facilities, and expertise to obtain suitable sample purity. Efforts in this task are aimed at reducing the preparation time for actinide mass spectrometry by using unique fluorination techniques developed at PNNL with milder NF_3 as the fluorinating agent to separate actinides from solids selectively and rapidly for direct insertion into the mass spectrometer.



Mass spectrum of evolved species from the reaction of TeO_2 with NF_3. Multiple TeF_X species are present due to electron impact ionization induced fragmentation. Isotopic resolution was obtained and corresponds to the correct natural abundance ratios for tellurium.

PN14061/2645

In FY 2014, a quadrupole mass spectrometer (QMS) with an electron impact ionization source was constructed and directly coupled to the gas outlet of a thermogravimetric analyzer (TGA), which was used to perform fluorination reactions between NF_3 and solid materials. For FY 2015, peer-reviewed manuscripts describing the instrument and acquisition of the tellurium hexafluoride mass spectrum were published in both the *Journal of Radiochemical and Nuclear Chemistry* and *Inorganic Chemistry*. Negative ionization source designs were tested, and reconfigurations of the TGA/MS design to accommodate higher boiling fluorides were tested with MoF_6. The instrument was later converted to a radiological instrument with the introduction of UF_6 into the system. A UF_6 spectrum was successfully acquired on the mass spectrometer using premade UF_6 compound. At the end of the year, experiments were planned to execute a full measurement of uranium hexafluoride from uranium oxides in the coupled instrument, and the final designs for the negative ionization source will be tested.

Advanced fuel development. During reactor accidents, volatile radioactive fission products are released to the environment, which created high levels of localized contamination and increased the global background. "Smart" fuels designed for accident tolerance would ideally incorporate additives to capture these products, preventing their release to the environment and maintaining them during accident site remediation. Because they are expected to persist throughout the fuel lifetime, the additives might have significant impact on fuel character and decisions for long-term used fuel disposition. This task examines the behavior of deliberately doped minor element inclusions in oxide fuels. In particular, metals that make up "white inclusions" were targeted because of their persistence and development that may be exploited as unique solid phases during irradiation.

We evaluated the viability of incorporating additional silver into the matrix at the fuel formation stage to capture fission iodine during irradiation for retention during accident conditions. Under this task, three methods were designed and investigated to incorporate silver into the uranium system: $UO_2(NO_3)_2{\cdot}AgNO_3$ direct recrystallization from solution, $UO_2C_2O_4{\cdot}Ag_2C_2O_4$ precipitation by addition of oxalic acid to the dilute nitrate solution, and $UO_2CO_3{\cdot}Ag_2CO_3$ precipitation at a 2:1 and 4:1 uranium-to-silver molar ratios. All methods were found to retain silver as small inclusions in the uranium oxide matrix up to 1200°C under air for up to 24 h without the loss of silver. SEM/EDS analysis was performed on the resulting oxides from each method, showing that different morphologies result for each species, forming cylinders, platelets, or spheres respectively, depending on the processing conditions used. The SEM results of these experiments and comparisons to real epsilon phases led to the publication of an article in the *Journal of Nuclear Materials*, and a full patent was filed covering the fuel fabrication methods.

Our efforts throughout FY 2015 continued to investigate the Ag-U-O system and included production of full Ag-doped UO_2 pellets at multiple levels of silver doping for fuel property testing. Powder X-ray characterization of the pellets revealed a new solid solution crystal phase fcc $(U,Ag)O_2$, raising additional questions about the mobility and retention of these minor elements in the fuel matrix. Additional efforts would explore the physical properties of these substitutional species such as thermal and electrical conductivity to characterize their in-reactor behavior.

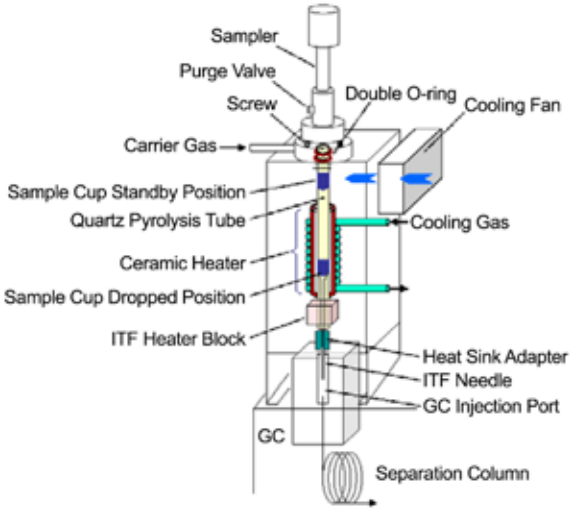
Molecular Fingerprint of ANFO Detonation

Carlos G. Fraga

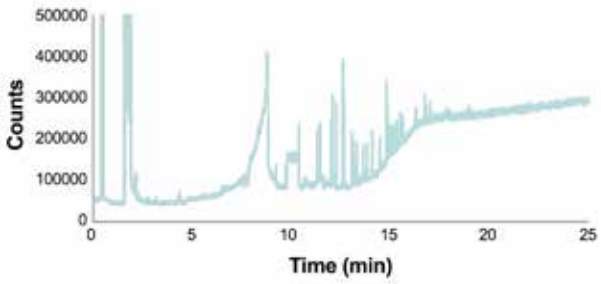
Our goal is to discover novel chemical signatures that may exist after the detonation of an ammonium nitrate (AN)-based explosive that may better identify the type and origin of explosive material used in an attack.

AN is an oxidizer widely used in improvised explosive devices (IEDs) and homemade explosives (HMEs). The chemical signatures in these materials may help investigators locate those responsible for IED and HME attacks. In this project, we are simulating the detonation of AN-based explosives through the thermal decomposition and combustion of both AN individually and AN fuel mixtures, followed by the characterization of their decomposition and combustion products in a laboratory environment.

Prior work demonstrated that numerous molecular species are released or produced from the thermal decomposition of blasting-grade AN with and without a hydrocarbon fuel. Most of these molecular species have not be previously reported and may be useful for determining the source of AN or for identifying an AN fuel explosion after detonation. The thermal decomposition and combustion of minute amounts of AN and AN fuel mixtures are being conducted using a pyrolysis unit capable of instantly heating a sample up to 1000°C. Gas chromatography/mass spectrometry (GC/MS) is then used to identify and quantify the molecular products produced from AN samples. Our objective is to use signature discovery principles and tools to discover forensic molecular products from the thermal decomposition and combustion of AN and AN fuel mixtures.



Schematic of a frontier multi-shot pyrolyzer furnace. The sample cup (blue) contains a few micrograms of a solid sample dropped into the ceramic heater where the sample thermally decomposes into gaseous products analyzed by a GC/MS



Molecular products produced from the thermal decomposition of 100 µg of tannerite AN using the pyrolysis GC/MS system. Furnace temperature was set to 550°C. Some of these products (i.e., GC peaks) may be useful for post-detonation forensics of AN-based explosives.

Our previous work estimated that the thermal decomposition of milligram amounts of AN is an acceptable approximation for modeling AN-based detonations. Our work resulted in the detection of the main chemical products (e.g., N_2, CO_2, NO, N_2O) produced from actual AN-based detonations. Additionally, we tentatively detected previously unreported trace chemical compounds such as alkyl nitriles, nitrobenzene, chloroform, and chlorinated hydrocarbons.

In FY 2015, we reproduced the findings from the previous year using a set of new AN samples. In addition, four compounds were verified and quantified using standards: chloroform, acetonitrile, pentane nitrile, and benzonitrile. We also designed and executed an experimental plan to determine if the variability from different AN manufacturers differs significantly in terms of the molecular products produced from AN thermal decomposition. Finally, we purchased and installed a commercial pyrolysis unit that can instantly heat a solid sample to temperatures of 400°C and above. These higher temperatures are needed to capture the entire range of chemical products potentially produced from an AN-based detonation. The higher temperature data will be required to extrapolate our laboratory work properly to an actual AN-based detonation.

In FY 2016, we will complete the statistical analysis of data from the FY 2015 screening study that tested the effect of manufacturer on the thermally produced products from AN. We will then design and execute several statistically designed studies to test the effects of AN grade, stock, fuel type, and heating temperature using the pyrolysis GC/MS system. Specific principles and tools will be used to select those products that are forensic signatures for AN detonations and origin.

PN15066/2741

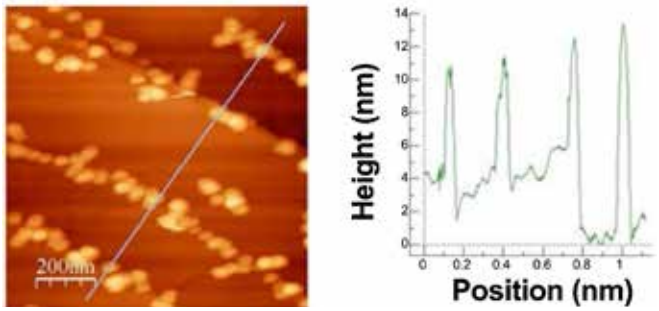
Novel Alloy Nanoparticle Materials for Catalysis and Energy Storage

Grant E. Johnson

This project is developing one-of-a-kind capabilities for the controlled preparation and characterization of alloy nanoparticles (NPs) of precise composition for applications in fuel cell catalysis and energy storage. The emerging capabilities are being applied to establish structure-reactivity relationships for alloy NPs.

We are focused on understanding how the size, elemental composition, surface density, and support interaction of alloy NPs may be tuned to improve catalytic activity, selectivity, and durability toward the oxygen reduction reaction (ORR). Custom modifications are underway on a unique nanocluster deposition system that will enable atomically precise control of the size and elemental composition of alloy NPs soft landed onto surfaces. A non-thermal physical synthesis technique is being developed to produce binary and ternary alloy NPs across a range of sizes and compositions that cannot be prepared using traditional solution-phase methods. New nanomaterials with promising catalytic properties are being discovered using this approach. A highly sensitive surface analysis technique is also being developed to screen the catalytic activity of NPs supported on surfaces at ambient conditions with minimal sample preparation. Achieving precise control of NP surface coverage and size is necessary to enable catalytic activity to be measured and calculated accurately as a function of metal loading and exposed surface area.

Employing simultaneous direct current magnetron sputtering of up to three independent metal targets in a single region of inert gas-aggregation, we produced anionic binary and ternary alloy NPs that contain a variety of transition metals (e.g., Fe, Co, Ni, V, Cu, and Pt). Mass-selected NPs were soft landed onto conductive glassy carbon (GC), highly oriented pyrolitic graphite (HOPG), and indium-tin-oxide (ITO) coated glass surfaces compatible with electrochemical analysis in solution using cyclic voltammetry (CV). We controlled NP coverage soft-landed onto substrates by measuring the ion current at the surface and adjusting the length of deposition. The NP surface coverage was determined by screening the surfaces with atomic force microscopy (AFM) following deposition. Using this approach, we demonstrated that on flat substrates such as GC, NPs locate randomly on the surface at low coverage. By comparison, on stepped surfaces such as HOPG, NPs nucleate preferentially along step edges, forming extended linear chains and leaving the terraces unoccupied. With increasing coverage, we observed with AFM that terrace sites fill until a dense layer of NPs is present across the HOPG surface. We also determined the size and size distribution of deposited NPs from the height measured frequency distribution. To validate the AFM observations, we analyzed the surfaces using scanning electron microscopy (SEM), which confirmed that at low coverage, the soft landed NPs are separated and located randomly on the flat GC surface. SEM results also verified that NPs line up at step edges at low coverage on stepped HOPG surfaces.



Left: AFM image of 8 nm diameter Cu NPs soft landed onto graphite; right: height profile across rows of Cu NPs aligned at step edges.

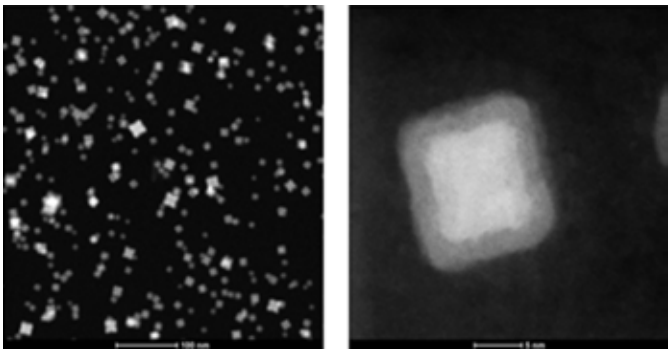
In addition to controlling the size and surface coverage of soft landed NPs, it is desirable to tune their morphology and elemental composition, which may be adjusted to reduce the loading of expensive precious metals (e.g., Pt and Au) and bring about physical lattice compression and strain as well as electronic structure effects that improve catalytic activity and selectivity. We employed systematic adjustments to the sputtering power applied to each of the three metal targets, the flow of sputtering (Ar) and buffer (He) gas, and the length of the gas-aggregation region to tune the morphology and elemental composition of NPs formed by magnetron sputtering and deposited them onto surfaces.

While the majority of NPs produced using this physical synthesis approach are spherical, we demonstrated that in the case of vanadium (V), it is possible to produce highly monodisperse nanocubes and soft land them onto carbon surfaces for subsequent atomic-level characterization using scanning transmission electron microscopy (STEM) at EMSL. As shown,

PN13005/2486

the wide-field STEM images established the cubic shape and similar size of the individual NPs on the surface. Atomically resolved near-field STEM images revealed sharp differences in contrast at the center and edges of the V NPs, indicating the presence of metallic V cores surrounded by V_xO_y shells. In addition, we achieved control of the elemental composition of alloy NPs. X-ray photoelectron spectroscopy (XPS) was used to confirm the incorporation of multiple metals into size-selected alloy NPs soft landed onto surfaces. A multimodal approach involving analysis by medium energy ion scattering (TOF-MEIS) and STEM confirmed the controlled creation of Pt-M (M = V and Cu) NPs with homogeneous alloy compositions and core-shell morphologies. In particular, STEM combined with elemental line scans using electron energy loss spectroscopy (EELS) demonstrated the formation of V-core Pt-shell NPs. These particles will make efficient use of a limited loading of precious Pt metal by concentrating it in the NP shell, not in the inaccessible NP core. The catalytic activity and stability of alloy NPs on GC was evaluated using CV under acidic solution conditions. A promising trend of increasing activity toward the ORR with incorporation of early 3D transition metals into the Pt-alloy was observed for NPs of similar size and surface coverage.

In FY 2014, an invited article was published in a special issue of the *International Journal of Mass Spectrometry* on the synthesis and characterization of metal oxide NPs that are promising candidates for applications in oxidation catalysis and electrochemical capacitors. A second invited paper was published in a Festschrift issue of the *Journal of Physical Chemistry A* that described the use of a flow reactor to control the distribution of metal NPs and to access reaction intermediates for soft landing and dissociation experiments. An invited comprehensive review article was published in *Mass Spectrometry Reviews* that highlights several aspects of this work. The technical accomplishments summarized in the preceding paragraphs were presented at the 2014 TechConnect World Conference in Washington, DC. Finally, our work was showcased in two invited university departmental seminars.



STEM images of 8 nm V NPs soft landed onto carbon.

In FY 2015, two full-length articles were published in the journal *Nanoscale* that described the synthesis and characterization of a variety of bare nanoparticles with controlled size, composition, and morphology as well as their catalytic activity towards reduction of O_2. An invited article about the influence of ligand length and saturation on the reactivity of soft landed gold clusters was published in a special edition of the *International Journal of Mass Spectrometry*. Aspects of this work were presented as an invited talk at the *Gaseous Ions Gordon Research Conference* and as a contributed talk at the *American Physical Society Meeting*.

An EMSL user proposal partially based on this work was awarded in collaboration with Purdue University that will utilize the novel capabilities developed in this project. The capabilities, publications, presentations, and collaborations resulting from this project are also providing the foundation necessary for the principal investigator to compete for funding through DOE's Basic Energy Sciences.

Predictive Understanding of Self-Assembly: Particle-Mediated Growth

Kevin M. Rosso

We are developing a fundamental understanding of particle-mediated growth of crystalline materials from aqueous solution. The primary goal is to develop appropriate new theory that identifies and encompasses the relevant chemical physics and couples length and time scales through appropriate projection schemes.

Despite its widespread importance in the precipitation and properties of earth materials and its prospect as a new synthesis pathway to tailored functional materials, there presently is no predictive modeling capability in mesoscale science space. This project will ultimately provide a foundation for predictive simulations on particle-mediated growth systems for comparison with self-assembly outcomes at various scales. An existing popular theory to describe energetics between two surfaces considers a simple balance between attractive and repulsive electrical double-layer forces, where parameters are strongly correlated with microscopic features like molecular structure and electron distribution. However, a complete understanding requires correlations over differing length scales in the energetics between two charged surfaces in aqueous electrolytes.

In FY 2015, we developed a model that encompasses the interfacial structure, quantum and atomistic statistical mechanics, and complexity of solution composition effects, emphasizing applicability to the solvent-separated particle capture regime. It is particularly key to the process because it defines the encounter frequency of aligned particles capable of successful attachment but is not well understood because it lies at particle separations too small for Derjaguin-Landau-Verwey-Overbeek (DLVO) theory yet too large for access by traditional atomistic molecular dynamics simulations. We used atomistic simulations based on classical density functional theory coupled with Lifshitz theory of van der Waals forces to describe interactions between anatase TiO_2 nanoparticles in a solvent separated state. The model includes microscopic ion-water hydration, ion-surface van der Waals and image interactions, mesoscopic interactions arising from density and charge density fluctuations in the electrolyte solution (excluding volume and ion correlation interactions), Coulomb interactions, and macroscopic particle-particle van der Waals interactions that account for ion screening of the zero frequency (static) van der Waals contribution.

The model does not rely on fitted parameters and was tested against experimental data for ion activity in bulk solutions 1:1, 2:1, and 3:1 electrolytes in the 0–2 M concentration range and against *ab initio* molecular dynamics data on specific ion adsorption at the air/water interface and water structure at solid surfaces. In the current formulation, the model does not yet treat chemical reactivity of particle surfaces, which limits its applicability to the range of interparticle separations above ~0.5 nm. However, the overall model is transferable to a wide range of nanoparticle/electrolyte systems and provides a basis for linking the solvent separated regime to the adhesion regime by prospective coupling to reactive molecular dynamics simulations for a comprehensive statistical mechanical model of facet specific interparticle interactions and oriented attachment (OA).

Our modeling results are consistent with experimental observations of most probable attachment along (112), occasional attachment along (001), and rare attachment along (101) at pH 3.12. More generally, they explain the driving forces for particle capture, the origin of facet selectivity and alignment forces in the solvent separated state, and barriers to attachment. In particular, the simulations revealed that the main attractive contributions to the interactions between nanoparticles are ion correlation forces with a typical range of 0.5–6 nm, static (zero frequency) van der Waals interactions between anatase particles across aqueous solution with the range of 0.5–10 nm for low concentration electrolyte and 0.5–2.5 nm for electrolyte concentrations above 1 mM, and short-range ion-surface dispersion interactions significant in the 0.75–1.5 nm range of interparticle distances.

Experimental work in FY 2015 was successful in developing oriented ZnO(001) nanoprobes and in measuring rupture forces between co-planar ZnO(001)-aqueous solution-ZnO(001) ternary interfaces *in situ* using dynamic force spectroscopy. In a technical first in science, the dependence of the rupture force on relative azimuthal orientation of the ZnO lattices interacting presumably across a few layers of aqueous solution was found to have a periodicity consistent with the hexagonal structure of this material and three-fold symmetry along (001), proving that forces consistent with OA were operative and measureable. Success in this area was also demonstrated for the system of mica(001)-aqueous solution-mica(001), a system that was further explored in terms of aqueous electrolyte type and concentration effects.

Dynamic force spectroscopy data were fit to a model to determine free energies of attachment, which will be used as a basis of comparison to our models as they develop to encompass the specific systems being measured. In FY 2016, we will continue refining the experimental protocol and perform a direct comparison of simulated force curves to experimental data.

PN14018/2602

Scalable Synthesis of Spinel Stabilized Metal Catalysts

Yong Wang

We are identifying, investigating, and developing new kinds of stable, active, supported metal catalysts that could be used by various industrial applications such as selective oxidation reactions and vehicle emission catalysts components.

Recently, we reported that $MgAl_2O_4$ support with controlled (111) facet can stabilize platinum catalysts under harsh reaction conditions. Conventional approaches via mechanical mixing of magnesia and alumina or co-precipitation of magnesium and alumina hydroxides typically lead to significant inhomogeneity in the amorphous mixture of magnesia and alumina, and consequently forming the spinel phase with inhomogeneity in local composition, structure, and morphology. We previously showed that $MgAl_2O_4$, synthesized via a novel non-aqueous approach capable to stabilize platinum particles during severe aging at 800°C. We revealed that the superior stability resulted from strong interactions between spinel surface oxygen and epitaxial platinum {111} facets. However, the approaches to synthesize $MgAl_2O_4$ spinel need more detailed investigation and understanding. For example, the solvent effect during synthesis, the surface properties of the formed products as well as their relationship need to be understood before scaling up the synthesis technology.

Our objective is to identify and develop a scalable synthesis approach of spinel $MgAl_2O_4$ synthesized via the novel non-aqueous approach and stabilize metal catalysts to understand the fundamental mechanism. These catalysts have attractive hydrothermal stability and have potential applications on several important industrial reactions such as biomass conversion and emission abatement. Ultimately, we expect to have a synthesis pathway identified and developed which can produce homogenous, hydrothermal stable and inexpensive $MgAl_2O_4$ catalyst support as well as its supported metal catalysts.

Conventional synthesized, commercial, and novel non-aqueous synthesized spinel $MgAl_2O_4$ were obtained. TGA and solid NMR of the synthesis precursor were done to investigate the mechanism of the crystallization process. XRD, NMR, BET surface area, NH_3-TPD, and zeta-potential were conducted to characterize the bulk and surface properties. Density functional theory (DFT) calculations were performed to determine the most stable surface orientation of spinel $MgAl_2O_4$. Platinum was loaded onto the three different $MgAl_2O_4$ spinel, respectively, using $PtCl_4$ as the precursor via incipient wetness impregnation. All samples were aging at 800°C for 1 day or 7 days, respectively. Chemisorption and TEM were applied to test the dispersion and stability of the platinum particles on the support. Catalytic reactions methanol oxidation and CO oxidation were conducted to verify platinum particle sizes and their activities.

We found that the non-aqueous novel synthesis approach is a continuous crystallization process by which conventional synthesis is two-stage crystallization. This finding was verified by NMR and XRD, while the nature of this difference will be investigated and analyzed. Zeta potential results helped verify the surface properties of $MgAl_2O_4$ obtained via unique synthesis approaches were different. The point of zero charge is pH 6.5 for novel synthesized $MgAl_2O_4$ and pH 10.2 for conventional. This result is one of the important causes for the different dispersion of Pt over different $MgAl_2O_4$ surfaces. NH_3-TPD results indicated the surface properties were very different. The novel synthesized $MgAl_2O_4$ might have less Al exposed than other samples since its NH_3-TPD curve is more close to MgO. DFT calculations show that the oxygen terminated (100) surface (100_O) of spinel $MgAl_2O_4$ is the most stable surface in low oxygen pressure conditions despite having the most strong interaction with metallic Pt or PtO_x. Further, Pt supported on novel synthesized $MgAl_2O_4$ has better dispersions and smaller Pt particles both before and after aging at 800°C. Both TEM and CO-chemisorption helped to verify this conclusion. Further, the catalytic activities on methanol oxidation and CO oxidation are the best respectively among all the different $MgAl_2O_4$ support. The surface charge helped improve the initial dispersion of Pt or PtO_x over the support, while the strong lattice matching effect help stabilize the Pt or PtO_x over the surface during aging.

For FY 2016, we will use ball mill technology plus water solution to treat synthesis precursors to help reduce the synthesis (especially in large quantities) cost and help us understand better the crystallization process mechanisms. The precursors will be subjected to different degree to hydrolysis and condensation before and after mixing. The structure and homogeneity of these reaction products will be studied by NMR, TGA, TEM, small angle scattering/diffraction, EXAFS and other techniques. *In situ* XRD and TEM and other techniques available will be used to gain an understanding of the early nucleation processes. After understanding the crystallization and properties of $MgAl_2O_4$, different metal loading approaches such as slurry impregnation, incipient wetness impreganation, and the colloidal method will be investigated. Additionally, stabilities and catalytic activities will be tested and analyzed.

PN15020/2695

Sequence-Defined Polymers Based on a New Backbone Architecture

Jay W. Grate

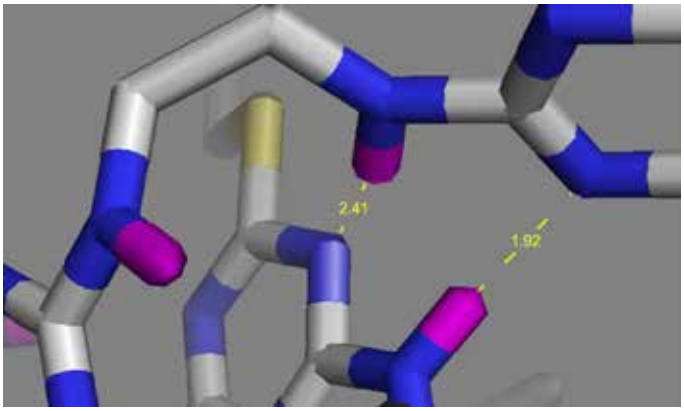
This project is investigating a novel bottoms-up self-assembly approach to achieve a controlled design and engineered polymer/nanostructure composites.

Sequence control in natural biopolymers such as DNA and proteins leads to tremendous structural diversity and functionality, such as material architectures, biocatalysis, molecular recognition, and transport across membranes. Realizing the same functionality in stable synthetic polymers will revolutionize materials science. Achieving this challenge will require both experimental synthesis and measurement of new polymer architectures with sequence control as well as molecular simulations to predict and understand macromolecular behavior.

Epitomized in nature by polypeptides and poly(nucleic acids), sequence-defined polymers are composed of a multiplicity of monomers, each monomer distinguished from one another by having a different side chain, and the various monomers are sequenced into the polymer in a predetermined order. In nature, sequence-defined polymers create biomaterials, encode information, perform biocatalysis, participate in molecular recognition, and shuttle species across membranes. More stable sequence-defined polymers prepared by chemical synthesis likewise have the potential to create tremendous structural diversity and functionality based on monomer sequence, if such synthetic polymer architectures can be developed. Such polymers will revolutionize materials science. The vast majority of synthetic sequence-defined polymers to date are either laboratory examples of the natural sequence-defined biopolymers, or close analogs based on similar structural units and bond-forming reactions. For example, pseudopeptides and peptoids both rely on amino acid structures and peptide bonds by analogy with polypeptides.

In this project, we have invented a new class of stable synthetic sequence-defined polymers based on monomers prepared from cyanuric chloride that is synthetically modified to have an R-group side chain. Additional reactions create aliphatic linkers between aromatic triazine rings. This monomer structure can be used to create sequence-defined polymers with no precedent in nature and little precedent in the chemistry literature; we call these triazine based polymers (TZPs). Our aims fall into the areas of synthesis, simulation, and *in situ* characterization of self assembly of these new sequence-defined polymers. Synthetic aims are to develop and demonstrate approaches that show diverse monomers with various R-group side chains can be prepared; various modifications of the core can be made to establish the first linker section; reactions that enable monomers can be linked into oligomers and polymers; and sequence-defined polymers can be made by solution and solid phase synthesis.

We successfully demonstrated the synthesis of molecular precursors that have a diversity of side chain structures. In addition to aliphatic and aromatic groups, we have created side chains with protected carboxylic acid and amine groups, which lead to ionizable side chains after deprotection. The latter side chains are important because ionizable side chains are significant in conformational structure. Molecular precursors with side chains have been sequenced into macromolecules using a submonomer solid phase synthesis technique that we developed for these TZP structures. The predetermined sequences range from arbitrary defined sequences to block copolymers, all of defined length.



Paired hydrogen bonds between monomers in a triazine polymer conformation.

In parallel with the experimental research, molecular dynamics simulations have been carried out that show intriguing patterns of noncovalent interactions between monomer units of the polymers. In single macromolecule studies, folded structures are observed with apparent similarities to peptide beta sheets or helices, stabilized by organized pairs of hydrogen bonds. In addition, simulations on pairs of molecules show similar patterns of hydrogen bonding, leading to nanorod structures.

These simulations show the potential for structural conformations to arise in solution, suggesting that TZPs will lead to functional macromolecules and self-assembled materials. Future work will focus on designing macromolecules specifically to investigate and demonstrate self-assembly behavior.

PN15018/2693

Simultaneous Electrochemical and Nuclear Magnetic Resonance Techniques for the Study of Electrochemically Active Biofilms

Ryan S. Renslow

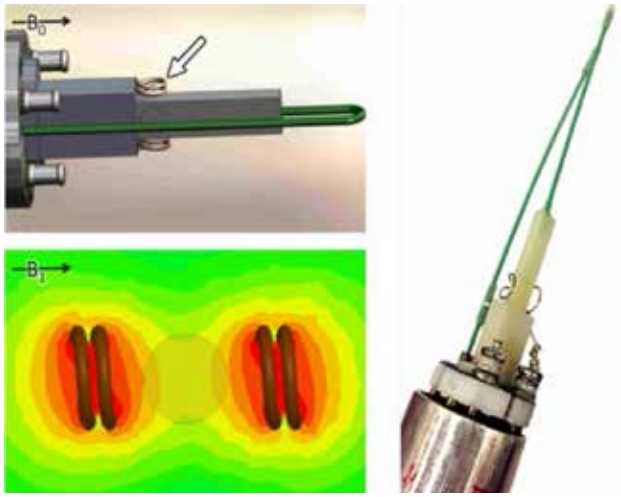
Understanding the microscale chemical gradients in electricity-producing biofilms and the ability of these microorganisms to use extracellular electron transfer can lead to novel applications in bioremediation, alternative energy production, and electrochemically stimulated synthetic biology to produce high value products.

Previous studies demonstrated that some bacteria are capable of transferring electrons derived from respiration to solid extracellular electron-accepting materials. Termed extracellular electron transfer (EET), this ability allows bacterial biofilms to use solid conductive substrata as a sole electron sink. The electrochemically active biofilms have numerous implications in biogeochemistry and microbial ecology, and they have been used in practical applications such as in marine-based microbial fuel cells to power oceanographic sensors and monitoring devices to extract energy and enhance chemical oxygen demand removal during wastewater treatment; to act as biosensors for nitrate/nitrite, glucose, and other chemicals; to desalinate water while simultaneously generating electricity; and for producing hydrogen gas via microbial-driven electrolysis. Understanding EET mechanisms will allow us to exploit and engineer this process for several beneficial applications, many of which are of interest to DOE, such as heavy metal and radionuclide bioremediation and electrochemically stimulated synthetic biology.

It is not known how microenvironments inside electrochemically active biofilms affect electron transfer mechanisms or if it is possible for a biofilm to use multiple electron transfer strategies simultaneously. We are addressing the role of microenvironments on electron transfer at a basic level, leading to enhanced applications of electricity producing biofilms. Combining nuclear magnetic resonance (NMR) with electrochemical techniques, we can explore electricity producing microorganisms non-invasively at the microscale.

To reach project goals, an electrochemical (EC)-NMR biofilm reactor was designed and optimized to allow simultaneous NMR and electrochemical techniques at high resolution and quick scan rates. To fulfill project objectives, we created a reactor with built-in reference and counter electrodes, improved the radio frequency coil, and incorporated electromagnetically shielded wire to minimize noise on the potentiostat lines. We formed a new reactor design using 3D printing technology that eliminates the optical window and has a ~60% smaller cross-sectional area (~40% smaller perimeter) with 50% less internal volume. A custom Faraday cage was built to enclose the potentiostats used for electrochemical techniques, improving the signal-to-noise ratio.

Two new NMR methods were developed that have significantly expanded the capability the EC-NMR setup. The point-resolved spectroscopy (PRESS) method enables up to second order shimming on a localized voxel, which increases the signal by 40% while improving the spectral resolution by improving peak resolution from between 14% and 24%. Second, a chemical shift selective imaging method was developed that enables 1D chemical shift selective imaging using slice selective excitation to choose a 1.5 mm thick plane centered on the explant that allowed rapid depth profiling of quantitative porosity. This method is an order of magnitude faster than previous depth profiling methods, though the spectroscopic dimension is not collected and the signal intensity is quantitatively proportional to excited nuclei concentration. These methods were used to study microbial mat and biofilm systems. The advances made during this project have been applicable to many fields, even outside of electrochemically-active biofilm research.



Optimized EC-NMR probe with disposable (3D-printed) biofilm reactors. Top left: Simulations of the EC-NMR probe to optimize the magnetic field generated by the radiofrequency coil. Bottom left: The fully constructed EC-NMR reactor. Right: The new probe coil offers an induced magnetic field 4× stronger than previous coils, enabling higher resolution and lower detection limits.

Work during this project has yielded over a dozen peer-reviewed papers and presentations at several conferences, two of which were invited international appearances.

PN13035/2516

Sub-Surface Catalytic Conversion of Oil Shale Kerogen into Shale Oil for Enhanced Oil Recovery

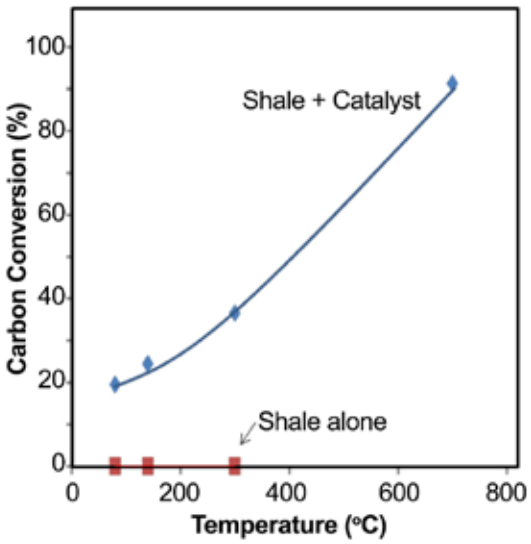
Vanessa Dagle

The potential of sub-surface catalytic conversion of shale deposits is a high risk, high reward strategy that could lead to a new platform of investigation beyond shale conversion such as the enhanced recovery of oil sands.

Although research work related to biofuels was tremendous over the last decade, advanced biofuels remain economically inviable. Hence, maximizing the availability of domestic fossil energy is crucial. The domestic production of shale gas and shale oil the last few years has been growing rapidly due to new drilling and fracking technologies. Shale oil is a mixture of hydrocarbons that could serve as fuel, being produced underground via kerogen conversion (trapped in the oil shale rocks) over "geological time." Novel technologies that could accelerate the underground kerogen conversion would help increase the yield of shale oil recovered in the United States.

In FY 2015, we conducted research with the possibility of accelerating the hydrocarbon transformations from a geological timeframe to something significantly shorter via sub-surface catalysis. Underground catalysis is very immature; therefore, it appeared essential to determine whether catalysis can be effective in underground conditions such as the low temperatures for catalysis (i.e., ~50–130°C) and the highly pressurized environment (i.e., ~5,000–10,000 psi). We have first demonstrated the feasibility of sub-surface catalysis at relatively low temperatures (≤140°C) as a way to recover shale gas and shale oil from the kerogen-containing shale rocks.

The image presents kerogen conversion represented as the carbon conversion as a function of temperature for a system at atmospheric pressure with and without a metal catalyst. As expected, kerogen is not converted to shale oil for temperatures ≤ 300°C in the absence of catalyst. Interestingly, when the shale rock is mixed with a catalyst, conversion of kerogen is ≤ 300°C. This result demonstrates that catalysts can help convert the kerogen into hydrocarbons fuel, and sub-surface catalysis seems feasible at low underground temperatures. Preliminary catalysts screening experiments indicated that cracking catalysts can efficiently convert the kerogen at relatively low temperatures (≤ 300°C). In addition, experiments using different shale and catalyst sizes of 30–200 mesh have indicated that smaller particles favor contact between the catalyst and kerogen-containing shale rock, which improves the hydrocarbon transformations. Indeed, 37% conversion was obtained for shale and metal catalyst particles size of 100–200 mesh compared to 5% for particles size of 30–60 mesh under the same reaction conditions (T=300°C, P=1 atmosphere). Hence, under realistic conditions (i.e., underground catalysis), it would be crucial for the catalyst to be in close contact with kerogen for catalysis to enhance the shale gas and oil recovery.



Evolution of carbon conversion as a function of temperature at atmospheric pressure under helium flow with and without a metal catalyst.

The results of experiments performed at atmospheric pressure appeared promising and encouraged us to conduct experiments under pressure to mimic underground conditions more accurately. To this end, experiments at 117 bar under N_2 flow at 300°C and for 5 days were conducted with and without catalyst. In absence of catalyst, no carbon conversion was detected. By contrast, for the experiment performed with a metal catalyst, carbon conversion was observed along the reactor bed. While only 5% of carbon conversion was obtained for the shale located on the front end of the reactor bed, 60% carbon conversion was achieved at the back end of the reactor bed. Note that the difference of conversion observed along the bed was attributed to a gradient of temperature.

We successfully demonstrated the feasibility of sub-surface catalysis as a way to recover natural gas and liquid hydrocarbons from underground at relatively low temperatures (≤ 300°C) and high pressure (117 bar). These findings will enable us to investigate the efficiency of this technology under pressure and in the presence of H_2O and/ or CO_2 to simulate better underground conditions.

PN15014/2689

Thermal- and Electro-Catalytic Routes to Conversion of Phenols to Fuels and Chemicals

Asanga B. Padmaperuma

This project seeks to compare the two pathways, offer insights that improve stabilization thermochemical (TC) and electrochemical reduction (ECR) methods, and ultimately make biofuels more affordable.

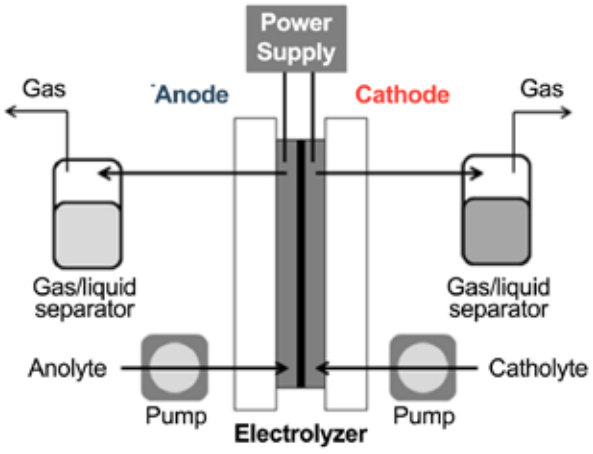
There is a lack of understanding about whether electrochemical processing can be used to economically upgrade bio-oils and how ECR conducted at ambient conditions compares with TC upgrading done at high pressures and temperatures. DOE seeks to develop processes for electrochemical stabilization and upgrading of bio-oil as a potential substitute for hydrothermal stabilization, the current state of technology.

In previous work conducted jointly with Idaho National Laboratory, we demonstrated electrochemical hydrogenation of reactive carbonyls and phenolics without adding elemental hydrogen. Compared with TC methods (>300°C, 2000 psig of H_2), the EC approach offers milder processing conditions (<100°C, <400 psig), decreased carbon loss (decreased coke formation; less cracking and hydrocracking), decreased H_2 usage (reducing equivalents generated *in situ*, light acids not hydrotreated), and reduced acidity. However, these benefits have not been demonstrated in head-to-head experiments. The aim of this work is to advance the science behind TC and ECR, identify ECR technology gaps, and compare EC and TC stabilization processes using the same metals, in one case as electrocatalysts and in the other as supported thermal hydrogenation catalysts.

Catalyst*	EC 25°C		TC 80°C		TC 140°C	
	Rate# (h^{-1})	WHSV (h^{-1})	Rate (h^{-1})	WHSV (h^{-1})	Rate (h^{-1})	WHSV (h^{-1})
Carbon	0.047	1.90	-	-	-	-
6% Cu	0.073	1.57	0.037–0.081	0.19	0.094–0.262	0.17
5% Ni	0.143	0.99	0.009–0.223	0.11	0.008–0.351	0.12
5% Pt	0.069	0.92	0.036–0.162	0.14	0.009–0.016	0.10
7.8% Ru	0.181	0.87	0.029–0.115	0.10	0.030–0.079	0.12

* TC: metal deposited on Norit ROX 0.8; EC: metals on graphite felt
\# Rate = g products/g catalyst/h

Benzaldehyde reduction results



Electrochemical reduction cell schematic

Bio-oil is a complex mixture of organic molecules. Of the carbon found in untreated bio-oils, over 55% is present as phenolic molecules, 20% is in the form of sugars, and nearly 5% is found in carbonyl-containing molecules. It is believed that the thermal reactivity of these three molecule classes decrease storage stability and shorten catalyst lifetime during upgrading.

This 3-month project investigated reduction of model compounds representing these three classes of molecules. Work was divided into two categories: conducting thermal hydrotreating using conditions that closely resemble the stabilization step in the current state-of-the-art for bio-oil upgrading and conducting electrochemical hydrotreating using a flow cell electrolyzer at ambient conditions.

Phenol, glucose, and benzaldehyde were chosen as bio-oil relevant model compounds for EC and TC processing. Using literature reports of thermal catalytic stabilization and prior experimental and theoretical ECR studies, electrodes and catalysts based on copper, ruthenium, nickel, and platinum were prepared. Electrocatalysts were deposited on graphite felt and thermal catalysts were supported on Norit ROX 0.8 carbon. Catalytic hydrogenation was conducted in the Avantium high-throughput flow reactor system at 140°C and 1200 psig of H_2. These conditions were used to mimic the stabilization step of bio-oil upgrading. Additional data were collected at 80°C. ECR was conducted in a flow cell built in-house for this project that has the capability to vary feed flow rates independently to the cathode and anode, collect liquid product samples at timed intervals, and analyze and quantitate evolved gases. Products from both routes were

PN15097/2772

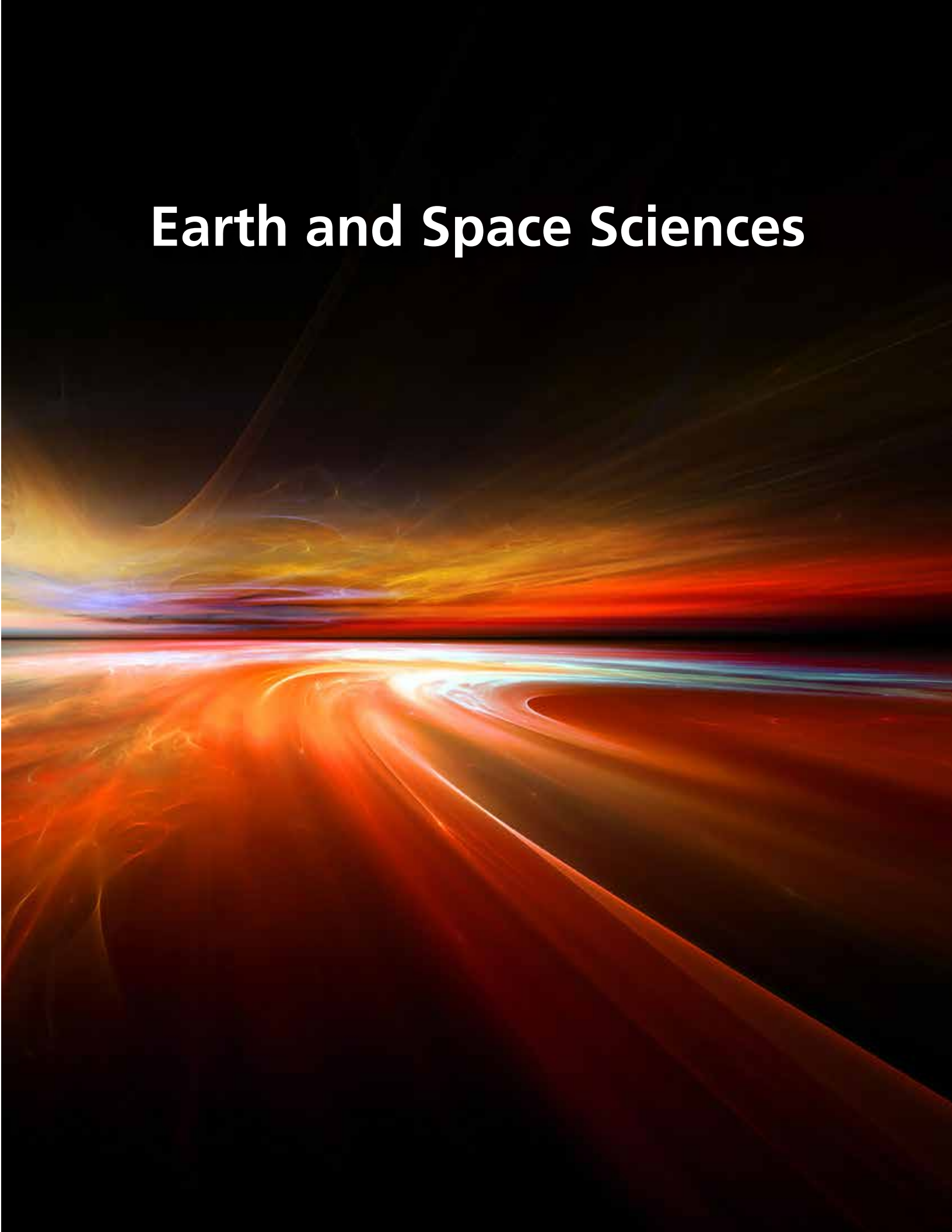
examined using GC and HPLC chromatographic techniques, and the choice of model compounds was based in part on straightforward analyses and quantitation of reduced products.

ECR converts benzaldehyde to benzyl alcohol as expected regardless of which electrode was used, including carbon. TC reduction, however, produced different products depending on the catalyst. Cu and Ni gave benzyl alcohol, Ru gave cyclohexanemethanol, while Pt at 140°C gave cyclohexanemethanol and at 80°C gave primarily benzyl alcohol. On a catalyst activity basis, ECR showed higher activity for the Ru and Pt electrodes. The Ni electrode was within the range obtained in TC treatment and the Cu electrode had lower activity. The Cu electrode, however, was not reduced properly and lost metal during the experiment.

TC reduction of phenol over precious metals such as platinum and ruthenium occurs with high conversion (near 100%) at 140°C. The major product is the ring hydrogenated product cyclohexanol. The conversion over nickel was 10%; copper and the Norit carbon showed no conversion. These results agree with what typically is seen in TC stabilization and hydrotreating. Surprisingly, EC showed almost no conversion of phenol, which is not consistent with the prior work done in a pressurized electrolyzer. This issue needs to be investigated further but may be related to the high space velocities used in the ECR cell.

This work has created the capability to conduct flow electrochemical reductions in a cell amenable for process optimization. Using the cell and existing thermochemical systems, we conducted a head-to-head comparison of hydrotreating of bio-oil relevant model molecules. Electrochemical reduction can have better catalytic activity than thermal reduction, can be conducted under milder conditions, and performed in locations that do not have ready access to pressurized H_2 gas.

Earth and Space Sciences



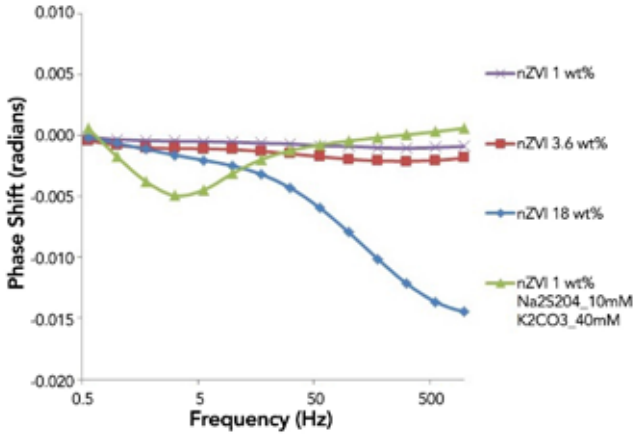
Assessment of Geophysical Tracers for Characterization of Natural and Stimulated Fracture Networks

Vincent R. Vermeul

This project seeks to evaluate the potential of using injectable zero valent iron (ZVI) solutions as a geophysical tracer for directly imaging fracture network distributions in the subsurface and measuring fracture surface area.

A major element of the SubTER New Sensors and Signals pillar is developing methods for characterizing natural and stimulated fracture networks. The primary objectives include determining the density and spatial distributions of fractures within the subsurface, interrogating fracture surface area, and providing for near real-time monitoring/imaging of fluid flow within a fracture network. It is well recognized that the use of engineered tracers is likely to play a key role in new technologies developed to meet this goal. Consequently, research and development on the use of tracers for fracture network characterization is specifically called out as one of the pillar target goals.

Tracers that enhance geophysical signals are one way to characterize fracture networks and monitor for changes that occur due to stimulation activities. PNNL is well positioned to contribute in this area. In particular, we have unique capabilities in 4D time-lapse electrical imaging that will be demonstrated next year as part of a collaboration with Sandia National Laboratory in a project focused on fracture change detection. This work has contributed to the development of capabilities that benefit this seedling and will help position PNNL for a leadership role in SubTER New Sensors and Signals.



Observed phase shift for various nZVI solutions. Note the large shift in magnitude and frequency at the maximum phase investigated (>500 Hz) for oxidized nZVI and ~5 Hz for nZVI treated with sodium dithionite to remove iron oxide coatings.

A series of laboratory experiments were conducted to evaluate the electrical properties of a suite of geophysical tracer formulations. Emphasis was placed on evaluation of micron- and nanoscale zero-valent iron particles in solution and comparison of these solution characteristics to a standard salt tracer. The experimental design was comprised of two elements.

Identify candidate tracers. Salt tracers were previously used in environmental applications to provide contrast in electrical properties within preferential flow zones that can be used for geophysical imaging of heterogeneities present within the subsurface. Micron and nanoscale metals particles are expected to provide improved contrast in electrical properties and thus improve our ability to image the subsurface. At least one salt tracer (for reference) and candidate metal particulate tracers will be identified for testing.

Evaluate electrical properties of identified tracer formulations. For each candidate tracer material identified, a series of tracer solution formulations were prepared and subjected to measurements of electrical conductivity over a spectrum of frequencies (spectral-induced polarization). These results were used to develop response curves for the various materials over a range of tracer concentrations and formulations.

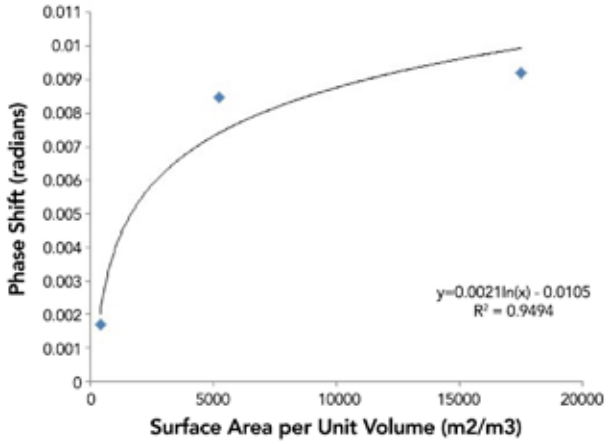
Results from this focused tracer evaluation indicate that the electrical conductivity characteristics of nano-scale ZVI are suitable for use as a geophysical tracer. Although a salt solution comparable to the salinity of seawater (35 g/L NaCl) provided a ~4× increase in electrical conductivity over that observed for nZVI, modeling results for a simplified fracture network indicated that this additional degree of conductivity contrast was not needed to facilitate effective geophysical imaging. In addition, nZVI provided other potential benefits that resulted in its selection over the standard salt tracer.

PN15086/2761

One benefit of using a particulate iron tracer is the potential for using spectral induced polarization (SIP) measurements (in addition to the contrast in bulk conductivity) to improve the fracture imaging capability. Electrical resistivity methods apply currents to a material and measure the resulting voltage changes. The SIP method collects information on not only the amplitude of the voltage signal but the phase delay over a range of frequencies. Each of the signal attributes are affected by the electrical properties of the solid and liquid components as well as interactions at the solid/liquid interface. In principle, a well-designed tracer can be used to isolate the two contributions to provide a means for characterizing and monitoring changes to the surface area of a fracture network.

Another benefit of nZVI is that unlike standard salt tracers, it is able to coat fracture surfaces which in turn can be used to interrogate fracture surface area. In this study, a preliminary evaluation of this effect was conducted using porous media coated with nZVI particles in simple column experiments. Several different porous media were used with different surface area characteristics to demonstrate that, as expected, frequency-dependent electrical properties were correlated with surface area. This relationship between surface area and electrical response is something that should be pursued in future work. Tracers and/or tracer suites and associated tracer injection methodologies that can effectively alter the electrical conductivity of fracture surfaces are needed. In addition, it must be demonstrated that the observed relationship between electrical properties and surface area will extend to fractured rock systems.

Data collected to date indicate that surface-mediated electrical property measurements are most sensitive under low surface-area conditions, indicating that this approach may be effective for interrogating fractured rock systems, which are inherently low porosity. This work represents an important area of research and a significant opportunity for improvement in the current state-of-the-art in fracture imaging technology.



The difference in phase shift between porous media saturated with tap water and nZVI tracer solution, plotted vs. the estimated surface area of the porous media.

Coupling the Spectral-bin Cloud Microphysics with Chemistry/Aerosol in WRF-Chem Framework

Jiwen Fan

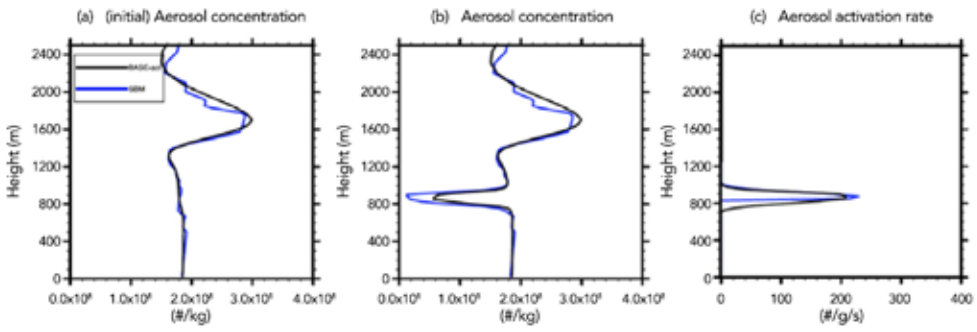
Our vision of this work is to develop a better modeling tool for studying clouds and aerosol-cloud interactions to improve understanding.

Clouds are one of the major uncertain quantities in climate simulations and prediction. Modeling clouds and aerosol-cloud interactions is difficult even at very high model resolutions due to our poor understanding of atmospheric chemistry and cloud physics. One of the main reasons for difficulties in simulating clouds is the imperfect treatment of the physics of interactions between water vapor and hydrometeors in clouds. Cloud microphysical processes are the key in this regard, and they are generally presented with a bulk or bin approach. Bulk schemes are commonly used due to low computational cost, but they are highly parameterized and the accuracy is compromised. Bin schemes can provide a more rigorous numerical solution and a more robust cloud microphysics representation, but require many more calculations. Simulations with bin schemes are often treated as benchmarks in studying clouds and aerosol-cloud interactions. Cloud microphysical properties also strongly depend on aerosol properties through their radiative and indirect effects. However, due to the expensive computation cost, the representation of the aerosol lifecycle in cloud models with bin cloud microphysics is very simple, which limits feedback mechanisms and the duration of simulations.

The rapid increase of computation power in the recent years allows the possibility to couple bin schemes with detailed chemistry and aerosol. In addition, for the same reason, applications of bin schemes to a large domain or a long simulation time become possible. Those applications require a good representation of the aerosol lifecycle. The objective of this project is to build an advanced modeling tool by coupling the Spectral-Bin Microphysics (SBM) model with a detailed chemistry/aerosol model based in the framework of the Chemistry version of Weather Research and Forecast (WRF) model (WRF-Chem), for providing benchmark simulations of both aerosols and clouds, which are very important for improving our understanding of aerosol-cloud-climate interactions.

We completed the coupling of the SBM with the sectional aerosol model the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) in WRF-Chem. The related work includes the following elements:

- Building an interface to connect the representations of interstitial and cloud-borne aerosol species in MOSAIC, in which four sections are used with SBM.
- Modifying aerosol activation. To calculate activation for aerosols of complicated compositions predicted by MOSAIC over four different sections appropriately, we convert the 33-mass aerosol bins in SBM to the critical supersaturation (Sc) bins, then map aerosols from MOSAIC into 33 bins based on their Sc in the interface. All particles from Sc bins with a Sc smaller than the model-predicted supersaturation are activated.
- Recoding aerosol resuspension, which is more physical by counting evaporated droplets calculated in SBM.
- Recoding in-cloud wet removal by calculating the droplet removal tendencies due to the transformation into rain, snow, and graupel in SBM.



Comparison of the vertical profiles of (a) initial aerosol number concentration, (b) time-area-averaged aerosol number concentration within the initial 10 min, and (c) averaged aerosol activation rate within initial 10-min between WRF-SBM-MOSAIC (black) and WRF-SBM (blue) with the prescribed aerosols. The simulated case is a stratocumulus from VOCALS.

The coupled modeling system is named as WRF-SBM-MOSAIC,

PN15043/2718

which we tested with a stratocumulus warm cloud case during the Variability of the American Monsoons Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx). We evaluated aerosol activation in WRF-SBM-MOSAIC with prescribed aerosols to compare with the activation of WRF-SBM. The results indicate that the aerosol activation in WRF-SBM-MOSAIC is consistent with that of WRF-SBM. In addition, aerosol resuspension and in-cloud wet removal were evaluated against the original WRF-Chem simulations in which a two-moment bulk microphysical scheme is used for bulk accuracy.

We completed a preliminary simulation for a deep convective cloud case occurring in South China to further evaluate the coupled modeling system and examine aerosol-cloud interactions. We plan to refine the model simulation and then evaluate it with observations. In addition, as of the end of FY 2015, this work produced two manuscripts: one will be submitted by the end of October, and the other (partly supported by this project) was submitted to the *Journal of Geophysical Research: Atmospheres*.

For this 1-year project, we reached milestones and accomplished the goal of building an advanced modeling tool by coupling SBM with the chemistry/aerosol models for studying aerosols, clouds and their interactions.

Determining Groundwater Residence Time Through Ultra-Low Measurements of ^{39}Ar and Other Radiotracers

Jill M. Brandenberger

We are leveraging PNNL's ultra-low background proportional counting (ULBPC) capability to validate using ultra-sensitive measurements of the noble gas radioisotope ^{39}Ar to constrain the age distribution of groundwater on intermediate timescales of 50–1000 years.

Quantifying the mean residence time (MRT) or age distributions of groundwater can be important for determining surface-groundwater interaction (recharge rates), evaluating connectivity of aquifers, verifying numerical groundwater models, and identifying depletion of groundwater aquifers critical for industrial/public use. MRT estimates require multiple environmental tracers covering age ranges of <50 (^{3}H/^{3}He, ^{85}Kr) and >1000 yrs (^{14}C). However, these established tracers do not adequately define the age distribution of groundwater aquifers recharging on intermediate time scales.

The need to refine the age distribution of groundwater is highlighted by the increasing number of groundwater resources that are depleted faster than they are being recharged. Depletion contributes to water shortages, increased costs, land subsidence, and water quality deterioration. Successfully building the ultra-sensitive ^{39}Ar measurement capability and attaining the scientific recognition for application to determining groundwater MRT requires the following steps:

- building efficient water degasification and Ar purification instruments (from FY 2014)
- enhancing the ULBPC measurements and increase gas transfer efficiency to ensure appropriate ^{39}Ar sensitivity for MRT (FY 2015)
- conducting verification sampling with U.S. Geological Survey to demonstrate the utility of adding ^{39}Ar to a suite of tracers used to determine age distributions (FY 2015)
- building an enduring reputation through creating an ^{39}Ar reference sample and conducting an international intercalibration exercise (for FY 2016).

Argon separation/purification bench

The activity of ^{39}Ar is 1.01 Bq/kg Ar ((8.0±0.6)×10−16 g/g), corresponding to an abundance of 0.808 ppq. Assuming a water temperature of 10°C, assuming water equilibrium with atmospheric air, and typical solubility of gases in water, the gas composition should be ~61.5% N_2, 3.6% O_2, and 2.5% Ar. Therefore, the target is to extract 4 L of Ar from 3000–5000 L of groundwater by pumping through a membrane degasification system. The membranes are plastic, hollow hydrophobic fibers with a vacuum used to strip dissolved gases from the groundwater. Water is fed around the outside of the hollow fibers, and a differential vacuum is applied to the fiber insides relative to the outside and dissolved gas passes from the water through the membrane into the inside of the fibers. The dissolved gas is then withdrawn using a diaphragm vacuum pump, to keep the sample isolated from pump oil or the atmospheric gases. The gas is collected in large aluminum coated plastic sample bags or compressed gas tanks. The system was designed to collect 400 L of gas in 5–8 h.

Purification: High recovery ^{39}Ar separation. A high recovery dual reflux pressure swing adsorption (PSA) system was developed at PNNL as a part of an enhanced Ar purification system. This new PSA increases Ar recovery efficiencies to 70–80% from gasses similar in composition to air, compared to the 20–40% achieved from commercial PSA oxygen generators. Similar to commercial PSA oxygen genera-

PN14007/2591

tors, the system maximizes a molecular sieve adsorbent (LiLSX) to separate N_2 from Ar and O_2 in the sample. The PSA is first purged with high purity gas containing 79% N_2, 21% O_2, and no argon. The PSA system is purged until the residual N_2 is at least two orders of magnitude lower than air, as measured by RGA. Therefore, atmospheric contamination from the gas separation process will be less than 1%.

Argon sample being loaded into the Ultra-Low-Background Counting System

Ultra-low-background counting system. The purified Ar sample cylinder filled from the purification bench is attached to the loading manifold and an empty proportional counter. The Ar gas is sent into the system where a SAES getter is used for the final clean-up. The Ar is then focused on a small liquid N_2 cooled cryotrap. Valves connecting the cryotrap to the detector are opened, and the proportional counter is filled by expanding the Ar gas as the cryotrap is heated. Used as a quench gas, methane is then added to the proportional counter such that the resulting gas mixture containing 10% methane and 90% geologic Ar (depleted in ^{39}Ar). The filled proportional counter is then taken to PNNL's ULBPC underground laboratory and counted. Each ULBPC must be characterized for modern Ar count gas and geologic argon. The modern Ar data is collected to provide an efficiency spectrum against which groundwater samples can be compared and used to calculate percent modern for each sample.

USGS verification sampling. PNNL is working with the U.S. Geological Survey (USGS) to conduct a joint publication on determining the age distribution of an aquifer in California based on several methods including ^{3}H/^{3}He (tritium), ^{39}Ar, and ^{14}C. Two wells in Fresno, CA were selected and simultaneously sampled for these isotopes in 2014. All samples were counted for 75 days and estimated ages and uncertainties demonstrate groundwater ages range 400–700 yrs since last contact with the atmosphere.

- Well #180 estimated to be 508 years at the 90% confidence interval with upper and lower bounds of +63 and -57.
- Well #170 estimated to be 565 years at the 90% confidence interval with upper and lower bounds of +66 and -59.

^{39}Ar international intercomparison. PNNL is leading the development of ^{39}Ar reference samples to share with international partners as part of an intercomparison study. International partners include the University of Bern and Heidelberg University. Activity levels for reference samples are 3 and 66× background, and a value of 1.6E-6 Bq/cm^3-Ar (STP) was used for calculations. PNNL arranged reactor irradiation of multiple potassium carbonate samples. The head-space gas above the powdered sample was then extracted and approximately 0.5 cm^3 (STP) of this gas was analyzed in a PNNL ULBPC to estimate specific activity. Based on this qualitative analysis, we estimated the specific activity of the ~4 cm^3 (STP) of material to be 1.25 Bq/cm^3 (STP). A stock target of 100× ^{39}Ar background was selected to allow sufficient activity for good counting statistics but also low enough activity to allow a modest dilution to obtain the reference samples. This procedure produced ~55 standard L of each activity to support the 2016 intercalibration study.

The project successfully demonstrated the first U.S. ULBPC ^{39}Ar measurement from several groundwater wells that have not been in contact with the atmosphere for 400–700 years. Key elements of this success include the development of a degasification unit and a higher efficiency dual reflux PSA that can provide up to 80% Ar recovery and is compatible with PNNL's separation chemistry used to remove radon and other contaminating species. In addition, the ULBPC were characterized for both atmospheric and geologic ^{39}Ar to determine accurately the intermediate age distributions with errors <25%, consistent with other groundwater tracers. Further characterization of the accuracy of these measurements is underway with the development of ^{39}Ar reference samples that will be shared with international experts during and intercomparison study in 2016. The next steps are to publish the intercomparison study results with the international partners and utilize the ^{39}Ar measurements as constraints for older and younger tracer methods to reduce groundwater modeling uncertainty and support the calibration of groundwater flow and transport models.

PN14007/2591

Development of Integrated Modeling Framework to Quantify Strong Interdependencies and Vulnerabilities Between Water and Energy in the Western Interconnection

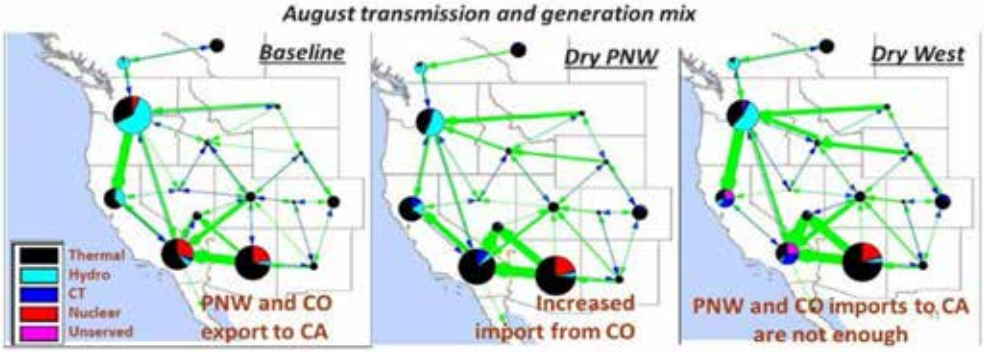
Nathalie Voisin

We are demonstrating and quantifying the dependence of the Western Interconnection on water availability and the role of regional hydro-climate variability on electrical grid performance.

The impact of water management on grid management extends across hydrologic regions through transmission systems. The dependence of the electric grid to water availability is neither well analyzed nor well communicated to decision-makers. Large-scale vulnerability assessments are usually performed for a baseline water year (current or future) or a specific drought. This approach does not provide insights into the full grid stress distribution that occur across many years and many states. At a smaller spatial scale, utilities generally assess vulnerability to extreme climate events for their specific system. Utilities who assume they are unique in experiencing climate event stresses at any specific time, relative to their neighbors, assume a diversity of water resources that may not exist as drought patterns may intensify spatially and temporally.

The outcome of the project is quantification of the energy management flexibility and highlights of opportunities for inter-regional joint water-energy management. This work contributes to emerging awareness of the role of inter-annual hydro-climate variability on the performance of the whole Western Interconnection grid performance. It leads to further research opportunities for assessing adequate resources planning under future climates and for increasing inter-regional coordination in joint water-energy management to meet the region's carbon emission objectives and to maximize the value of the regional hydro resources.

In this project, we estimated the impacts of the water availability on the electricity generation and transmission in the western U.S. grid for a range of historical water availability combinations. We softly coupled PNNL Platform for Regional Integrated Modeling and Analysis (PRIMA) integrated water model, which includes climate, hydrology, routing, water resources management and socio-economic water demand models, into a grid model (production cost model) and simulated 30 years of historical hourly power flow conditions in the western U.S. grid. A water scarcity grid impact factor was developed which corresponds to existing drought severity indices but specifically reflects the impact of the water availability on grid generation capacity. Using the water scarcity grid impact factor and an integrated modeling approach, we derived a grid stress function that demonstrates and quantifies the dependence of the western electric grid reliability to water availability and regional inter-dependencies. We also conceptualized inter-regional reliability spaces which indicate how far a region is from failing to meet its energy demand based on its water availability and level of demand. The



August regional power transfers and generation dispatch for different water year case studies: baseline, dry Pacific Northwest, and dry West. Green lines represent peak hour flow and direction of transfer; blue lines represents off-hour transfers. No two droughts are alike. The dry West (right-most panel) drought would drive to a 6% unserved energy demand in the absence of contingency plan in energy management.

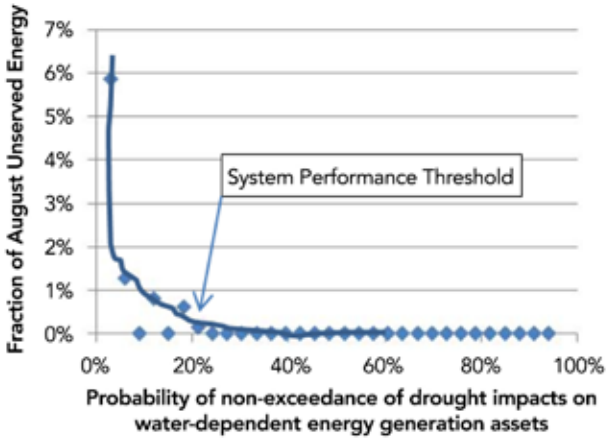
PN15026/2701

inter-regional aspect of the reliability space is a platform for inter-regional water-energy trade-off opportunities.

Results indicate a clear correlation between grid performance (as quantified in unmet energy demand and increased production cost) for the summer month of August and annual water availability. Within historical inter-annual climate variability the operational peak capacity meets NERC's WECC-wide requirement. However, without contingency plans on water uses or generation portfolio requirements, there is a 3% chance that under historical inter-annual climate variability, the grid as of 2010 is unable to meet 6% or more of its August energy demand, with the failure to meet the demand located mostly in California. There is a 21% chance of not meeting 0.1% of the load in the western U.S. grid.

The regional variability in water availability significantly influences grid performance and could provide trade off opportunities in times of stress. Regional drought patterns were identified with uncertainty range for providing predictability on the vulnerability of the grid. California hydrologic region is the main source of vulnerability of the grid while the Pacific Northwest region is the main contributor to mitigating grid impacts of California droughts. This finding is positioning the Northwest as a major virtual water (hydropower, thermo-electric plant with wet cooling) trader in the future. Consideration of water scarcity on transmission utilization and capacities are expected, given the increased dependence on inter-regional power transfers.

The proof-of-concept of the grid level and regional reliability spaces as a function of hydro-climate dependent indices is opening opportunities to develop more informed joint water-energy management in terms of flexibility across regions and also across water uses for a more resilient, reliable, and sustainable grid and hydro system. Energy management will likely turn toward inter-hydrologic region water-energy tradeoffs for adapting to future conditions. The potential for inter-regional water-energy tradeoffs will require increasing levels of planning and management sophistication for entities responsible for management of individual hydrologic regions. In addition, the reliability assessment may not fully account for drought conditions and the planning for expansion of transmission and infrastructure is suboptimal if the range of inter-annual and inter-regional variability is not well represented in the analyses.



Inter-dependency of western electrical grid performance and regional water availability represented as a grid stress function; it represents the risk to the Western Interconnection as it associates multiple levels of potential unmet energy demand with a range of probabilities of occurrence. The system performance threshold indicates the drought severity level (based on water availability across load regions), beyond which there is likely to be unmet energy demand if a contingency plan (change in energy management) is not in place.

Enhanced Sediment Geochronology Achieved Using Ultra-Low Background Materials and Ultra-Sensitive Detection Capability

Gary A. Gill

This project will produce new and enhanced capabilities that will have significant impact on environmental geochronology and other low-background radiation measurement applications, significantly advancing PNNL as a national leader in these areas.

A gap exists in age dating of environmental systems (e.g., sediment, trees, groundwater) between ~100 and 1000 yrs, limiting our ability to understand ecosystem changes as a function of climate and human drivers. Thus, the objectives of this project are to:

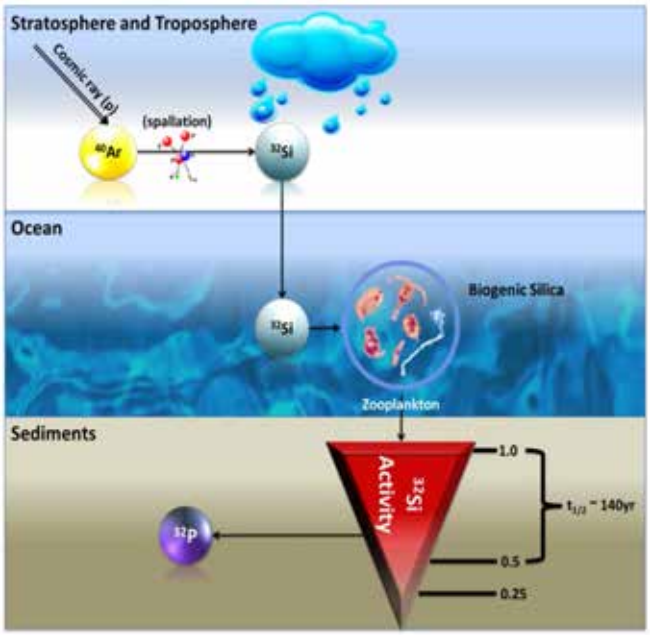
- produce a new sediment geochronology tool based on highly sensitive radiometric dating using ^{32}Si (half-life ~140 yrs)
- develop the world's lowest-background beta detectors utilizing new low-background plastics to enable the ^{32}Si age dating method
- demonstrate ^{32}Si age dating with Puget Sound sediment cores in the 100-1000 year age bracket.
- potentially make a new, high-precision measurement of the ^{32}Si half-life.

This project will produce a new sediment geochronology tool based on ^{32}Si (half-life ~140 yrs) that will be useful in the time frame of 100–1,000 years, a time period not currently covered adequately by other radioisotopic geochronology methods. This capability will be achieved through the development of new ultra-sensitive beta detectors and identification and manufacturing of detector component materials with low-background signals. In addition, we will demonstrate this capability by conducting a geochronology (age dating) of sediment cores collected from Puget Sound through a comparison to radiochemical geochronology using ^{210}Pb.

The project began in FY 2013 and was organized into three components: a geochemical task involving isolation of ^{32}Si (^{32}P) from sediments for radiometric detection; development of a highly sensitive and low-background beta detector; and determination of ^{32}Si half-life.

Sediment geochemistry. A major effort in FY 2015 involved the processing of enriched sediments from Sequim Bay using optimized chemistry procedures and measuring chemical yields and radiogenic decontamination at each step. The final phosphorous yield was 66% with no measureable Si based on ICP-OES analysis.

The final P solution was prepped for a final CASCADES measurement with the results indicating a weak positive for thorium decay chain isotopes (^{228}Ac, ^{212}Pb, and ^{208}Tl). Efforts are still taking place in regards to interpreting these values against critical limits for CASCADES. However, the associated background from the sample may still be unacceptably high and will be determined using the BIDS detector when operational in the shallow underground laboratory at PNNL. In the meantime, additional chemical steps will be evaluated to reduce the current radiogenic background further as well as decrease the final volume of the P fraction for easier BIDS detector sample preparation.



^{32}Si is produced in the troposphere by cosmic radiation; it is removed from the atmosphere in wet and dry deposition, incorporated into plankton, and removed to sediments (biogenic silica). ^{32}Si activity decreases with depth (half-life ~140 yrs) in sediments providing a means to age date sediment layers. The daughter of ^{32}Si, ^{32}P, is quantified, as it has a higher activity and is in secular equilibrium with ^{32}Si.

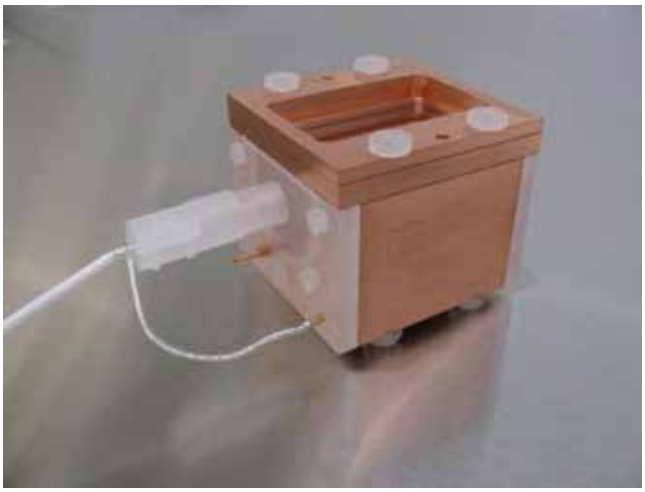
Ultra-sensitive BIDS detector development. The background performance and

PN13018/2499

detection efficiency of BIDS Prototype low-background counters were studied in FY 2015. Detector background performance in the PNNL shallow underground laboratory indicate backgrounds on the order of 40 counts per day (cpd), higher than the background goal. These tests were performed in a pre-existing shield system, and a significant fraction of the remaining backgrounds are attributed to un-tagged cosmic radiation; the right hand column presents anticipated performance with improved cosmic tagging. A new shield system, designed for high cosmic rejection, is currently being completed and will be available for testing at the beginning of FY 2016. New detector housing was also designed and fabricated to eliminate observed high-frequency noise pickup.

Initial FY 2014 measurement of the detection efficiency was ~40% for two detectors in 4π configuration, significantly lower than desired. During FY 2015, the sample mounting geometry was revised, and subsequent measurement indicated ~100% detection efficiency for ^{32}P. An article based on this work has been accepted for publication in the *Journal of Radioanalytical and Nuclear Chemistry*.

Significant improvements in the separation of biogenic silica from bulk sediments and extraction of 32-Si from the biogenic silica enriched sediments were achieved in FY 2015. These improvements resulted in a significant reduction in the natural background radiogenic signal present in the sediments. The performance of the beta detector with ^{32}P standards was exceptional, yielding essentially 100% detection efficiency. This performance bodes well the ability to detect ^{32}P signals derived from ^{32}Si decay in sediments. Several samples from a sediment core collected from Puget Sound have been processed and wait for counting once the new shield system is installed in the underground laboratory. We anticipate that once these samples have been counted, this information will provide the basis of a proof-of-concept paper for an environmental biogeochemistry journal and gain PNNL recognition for this unique radiochemical age-dating technique.



Assembled low-background detector

How Do Non-linear Microbial Processes Lead to Linear Ecosystem Fluxes?

Katherine E.O. Todd-Brown

This project incorporates new microbial measurements and understanding into soil carbon models, bridging the gap between microbial processes and ecosystem observations.

Modeling soil carbon dynamics is critical to predicting how much carbon dioxide will be in the atmosphere to drive future climate change. Soil carbon models have remained essentially unchanged for decades. These models partition soil carbon into 1–9 pools; carbon leaves these pools at a rate proportional to the amount of carbon in the pool (i.e., first order linear decay); some of the carbon leaving these pools is diverted to other pools and the rest leaves the system as carbon dioxide. Most research since the 1980s has focused on generating environmental sensitivity functions for the decay rates or physical/chemical characterization of the soil carbon pools. This model type tends to statistically fit observed soil carbon emissions. However, despite extensive attempts to characterized the environmental sensitivity, parameters must be re-calibrated for each location making it difficult to confidently generalize these models to global projections.

In the past 15 years, new microbial characterization methods have led to a growing interest in the biogeochemistry community in microbially explicit decomposition models where soil carbon must first pass through a microbial pool before leaving the system as carbon dioxide. These models are appealing not only because they can describe a more fundamental understanding of soil decomposition, but also for their potential to incorporate new genetic and other 'omic measurements. However, there is an issue of scale: carbon decomposition occurs at the pore-scale (<1 mm^3), and the fluxes of interest occur at the ecosystem-scale (>1 km^2).

If we are going to apply our understanding of microbial dynamics to carbon decay models, we must first develop high-resolution models and then scale to coarser resolutions of interest. This project emphasizes both scale-specific model development and explicit scaling linking process understanding with observations and global projections.

Although the project began mid-year, there are already several notable developments for FY 2015. We are preparing a manuscript for journal submittal into the next fiscal year that maps the processes and mathematical formulation for a novel high-resolution soil decomposition model. The work draws on a dozen collaborators across PNNL, other DOE laboratories, and academia, and is the first proposed model that incorporates biological, chemical, hydrological, and soil physics into a single coherent framework. This work has already attracted the attention of the scientific community through an invited presentation at the Ecological Society of America on this topic in August 2015.

In addition, work with colleagues is being performed to collect data from soil incubation and litter bag mass loss studies to conduct a model power study. This study will build on the first order linear models and endeavor to determine how many soil carbon pools there are and what connections between those pools are statistically supported. Historically, these first order linear pool models have been hand-tuned by model developers. While there are some recent examples of a more formal data integration for single sites, this scenario has not be broadly studied across sites yet. Currently, six studies have been collected that comprise hundreds of data points, and work is progressing with collaborators to expand on these data sets. The analysis methods are currently being prototyped, and a manuscript submission is expected in the next year.

In FY 2016, we hope to implement the high-resolution decomposition model laid out in the framework manuscript described previously. This effort will entail collaboration with hydrologists at PNNL to combine existing fluid dynamics models with cell growth models at <20 microns, a high resolution that will allow us to comfortably assume "well-mixed" conditions and directly import models developed for batch cultures in the lab into the highly structured environment found in soils.

Fundamental issues that will be addressed with this pore-scale decomposition model include determining the relative contributions of substrate heterogeneity, spatial structure, and microbial diversity in "smoothing out" non-linear microbial kinetics. We will also consider how biomarkers (i.e., 'omic measurements) are linked to microsite heterogeneity. These are critical questions to answer if we are to link new microbial and chemical measurements with biogeochemical fluxes.

In the final year of the project, we will link the high-resolution microbial process model with the statistical power study described above via explicit scaling techniques. These techniques will likely include methods from applied mathematics (i.e., bifurcation, steady state, and order of magnitude analysis), statistics, and other numerical methods. To our knowledge, this is the first study to explicitly scale a high-resolution soil decomposition model to coarser spatial and temporal scales. This explicit scaling will finally allow microbial measurements and characterization to inform ecosystem level flux predictions in a predictive and mechanistic manner.

PN15094/2769

Identifying Cloud Phase States from Multiple Remote Sensing Observations

Laura D. Riihimaki

Cloud feedbacks remain one of the greatest uncertainties in climate models. A more quantitatively rigorous identification of cloud phase from remote sensors can improve understanding of cloud processes, leading to better accuracy of cloud predictions from global climate models.

Between atmospheric temperatures of 0 and –40°C, clouds can contain ice crystals, super-cooled liquid droplets, or both, impacting how clouds influence the energy budget of the atmosphere. DOE's Atmospheric Radiation Measurement (ARM) Climate Research Facility makes multiple remote sensing measurements capable of providing information about the vertical distribution of cloud phase, though each is more effective in particular conditions. Current operational phase identification algorithms exist in the literature; however, they do not use all the available information from ARM remote sensors that has shown to be useful, nor do they give quantitative assessments of the uncertainty of the phase determination in given conditions. In this project, we are leveraging statistical and big data tools developed at PNNL to identify data signatures to formulate a phase detection algorithm that includes additional information from radar Doppler spectra and a more rigorous assessment of algorithm fidelity in a given situation using Bayesian networks.

In the initial seed-phase of this project, we created a merged dataset from the Barrow, Alaska ARM site that puts measurements from multiple remote sensing instruments (lidar, cloud radar, balloon-sonde, etc.) into a common temporal and spatial resolution. This scenario allows us to compare the information content from multiple remote sensing instruments during a field campaign that also has *in situ* validation data of cloud phase gathered from aircraft flights through clouds.

The green laser beam from the high spectral resolution lidar is visible in the dark sky at the Barrow, Alaska ARM measurement site. The polarization and intensity of the backscattered light help identify layers of super-cooled liquid in arctic clouds.

We applied the current best operational phase classification algorithm from the literature to this data as our control algorithm. This phase classification is based on only three moments of the radar Doppler spectra (reflectivity, mean Doppler velocity, spectral width) but can miss information from Doppler spectra with multiple peaks, an indicator of mixed-phase conditions. We examined this initial phase detection method with a more detailed radar measurement dataset and found indications of phase misclassification. For example, only 2/3 of cases with multiple peaks in the radar Doppler spectra were classified as mixed-phase instead of all cases, as we would expect. Also, some liquid-identified cloud cases gave radar reflectivity values that were too high, another likely indication of phase misclassification. These preliminary results were presented mid-summer at the American Meteorological Society Cloud Physics meeting.

In FY 2015, we developed an improved cloud phase algorithm using a Bayesian framework that indicates the signature quality for a given set of available measurements. For example, lidar depolarization ratio can be used to determine cases of super-cooled liquid water with high confidence. However, the lidar is attenuated quickly in clouds that contain water, so it is not always available to help determine cloud phase. After exploring statistical relationships between new moments of the radar Doppler spectra using a combination of clustering algorithms and visualization tools, we chose two lidar and eight radar variables to develop the algorithm.

We identified periods of liquid, ice, mixed-phase (liquid and ice), and snow conditions with which to train the algorithm. Using half of this ground-truth data set, we fit normal functions to the 10 chosen parameters and applied these to the remaining measurements using Bayesian probability to test the algorithm accuracy. This cross-validation showed 98%, 94%, 88%, and 88% agreement for ice, liquid, mixed, and snow categories, respectively, indicating a high ability of the algorithm to identify the correct cloud phase. Sensitivity tests showed that including the additional radar variables allowed better identification of mixed and snow categories when lidar data were not available.

The results of this work were composed as a journal article currently under review. Additionally, the results were presented at the American Geophysical Union in December 2014, the DOE Atmospheric Systems Research PI meeting in spring 2015, and the Radiation and Climate Gordon Research Conference in summer 2015. Further work in developing and using the algorithm to improve our understanding of cloud phasing is also underway in a follow-on project.

PN14084/2668

Measuring and Modeling the Climatic Effects of Brown Carbon Atmospheric Aerosols: Developing an Integrated Capability

John E. Shilling

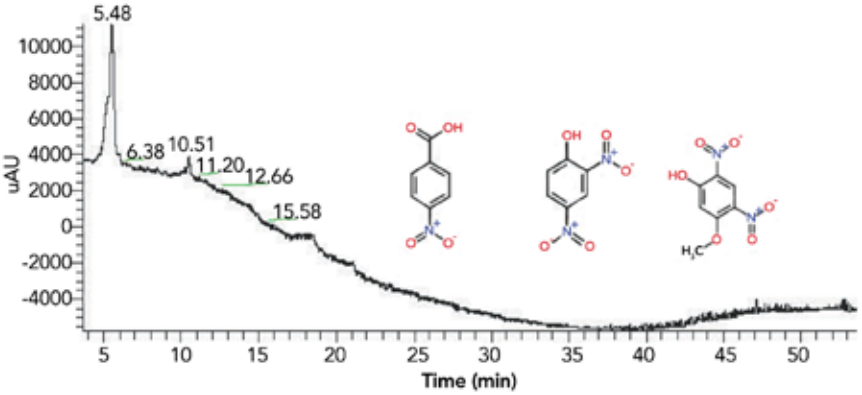
This project will lead to new insights into the conditions under which brown carbon aerosols form; the processes that govern time-evolving chemical, physical, and optical properties; new methods for efficiently representing the processes and properties in climate models; and an evaluation of the impact the particles have on climate.

Aerosols represent one of the largest sources of uncertainty in understanding and simulating future changes in the earth's climate. Aerosols affect the climate system by scattering and absorbing radiation, thereby affecting regional and global energy balances, and indirectly by altering cloud properties and lifetimes. It is commonly assumed that organic aerosols contain only non-absorbing materials and therefore have a predominantly cooling effect on climate. However, increasing evidence suggests aerosol aging may lead to the formation of light-absorbing organic compounds (i.e., brown carbon), which could exert a significant climatic impact currently not captured in climate models.

Unraveling the chemical composition, physical properties, and potential climatic effects of brown carbon aerosols is a multidisciplinary challenge that spans spatial scales ranging from individual molecules to the entire globe. We are developing a fundamental, molecular-level understanding of the chemical and physical processes governing the growth and aging of brown carbon aerosols in the atmosphere; determining how the resulting chemical and physical transformations affect the radiative properties of the species involved; and evaluating the significance of these processes for global and regional climate by developing parameterizations that encapsulate this new understanding and testing these parameterizations in climate models. Incorporating brown carbon formation processes will improve the accuracy of climate models, leading to better predictions of future climate.

In FY 2013, we found that aerosol particles were white (non-absorbing) when produced under low-NO_x conditions and brown (absorbing) when produced under high-NO_x conditions. Aerosol samples were collected on filters, and the samples from experiments were collected and analyzed using nanospray desorption electrospray ionization coupled to a high-resolution mass spectrometer at EMSL. These results indicate the incorporation of NO and potentially NO_2 with concomitant loss of one water molecule into the primary oxidation products of trimethylbenzene. We also performed an exploratory scoping exercise using the Community Earth System Model (CAM5) global climate model to estimate atmospheric and surface forcing that would arise if organic aerosol were much more absorbing than usually assumed by climate models.

In FY 2014, we extended our laboratory studies to a wider range of precursors and photochemical conditions. We investigated the optical properties of organic aerosol produced from the photooxidation of alpha-pinene, toluene, and isoprene under both high-NO_x and low-NO_x conditions. Optical absorption for all precursors is enhanced under high-NO_x conditions; however, aerosol produced from isoprene and alpha-pinene showed little absorption even under high-NO_x conditions. Aerosol formed from toluene under high-NO_x



Analysis of absorbing organic aerosol produced from the photooxidation of toluene under high-NO_x conditions. Liquid chromatography separation followed by ultraviolet-visible spectroscopy detection and mass spectrometric detection is used to identify specific molecular products responsible for aerosol absorption (browning).

PN13073/2554

photochemical conditions showed the largest absorption, with a four-fold increase relative to trimethylbenze aerosol produced under similar conditions. The use of acidic sulfate particles did not significantly enhance absorption of secondary organic aerosols (SOA) produced from any precursor. The combination of unique techniques allowed us to identify the specific molecules responsible for light absorption that include nitro-aromatic species substituted with acid or phenol groups. The results again indicated that incorporation of nitro groups during toluene oxidation were the key to producing chromophores.

In FY 2015, we finalized analysis of the detailed molecular composition of brown carbon SOA and the molecular modeling of the proposed chromophores. A manuscript describing these results was written and published in *Physical Chemistry Chemical Physics* and was featured as the journal's cover. A small number of laboratory studies were conducted to determine how the optical properties of the brown carbon SOA evolve with exposure to UV light and photochemical oxidation. We found that the light absorption becomes less efficient as the particles age. We also found a small enhancement in the light absorption properties of particles when toluene and isoprene SOA are co-produced in the presence of NO_x.

We made significant improvements in the way brown carbon aerosol is represented in climate models during

FY 2015. We changed the fundamental assumptions about aerosols used in the radiative transfer code used in CESM and ACME models to make it easier to study and describe the impact of brown carbon (and indeed all other) aerosols on climate. Rather than use the simple assumption that all aerosol components are homogeneously mixed within the particle, we characterized their properties using a much more realistic assumption: that the aerosols can be represented as a shell of condensable species (e.g., brown carbon SOA) around an insoluble core (mineral dust, soot, etc.). The particle properties were specified as function of the particle size, core size, and complex index of refractions of shell and core components. We used a costly but accurate Mie code calculation to produce estimates of scattering, asymmetry factor, and absorption for 30 wavelengths in the long and shortwave spectrum for three aerosol modes comprised of different aerosol species. The Mie code was run for a total of 256 different configurations to produce a dataset that can be used to build a surrogate model (a high dimension polynomial) using Polynomial Chaos Expansion methods. The resulting surrogate model was then used to estimate the aerosol optical properties for the CESM radiative transfer code. The surrogate model explained better than 95% of the variance of the Mie calculation (i.e., it is very accurate and very fast).

We are in the process of conducting longer model simulations to assess the impact of the new treatment on the model climate and compare the aerosol optical characteristics (spectrally resolved extinction and scattering) to observed aerosol properties. Our plan is to incorporate this improved characterization of aerosol optical properties produced in studies as an integrating activity of the laboratory, theoretical, and modeling components of this project. We are also discussing our results in a paper to be submitted during the next fiscal year that addresses the importance of brown carbon in a shell core framework and describes the impact of an improved (modeling and chemical) understanding produced by the project on aerosol forcing and climate response.

Nonstationary Climate Considerations - Climate and Hydrology

David R. Judi

Tools and methodologies for global and regional climate model projections to develop local-scale, actionable information will enhance the resilient design of communities and critical infrastructure under non-stationary conditions.

Flooding has been observed to become more prevalent and is expected to worsen with a changing climate, including potential increased precipitation and snowmelt runoff. For example, some coastal areas frequently experience flooding resulting from relatively minor precipitation and tidal events because of local changes in sea level. Inland areas have also become more vulnerable to flooding. The majority of the United States has seen an increase in short duration, high intensity precipitation events and these events are expected to increase in frequency and intensity. The observed and projected changes in precipitation are commonly referred to as a non-stationary climate.

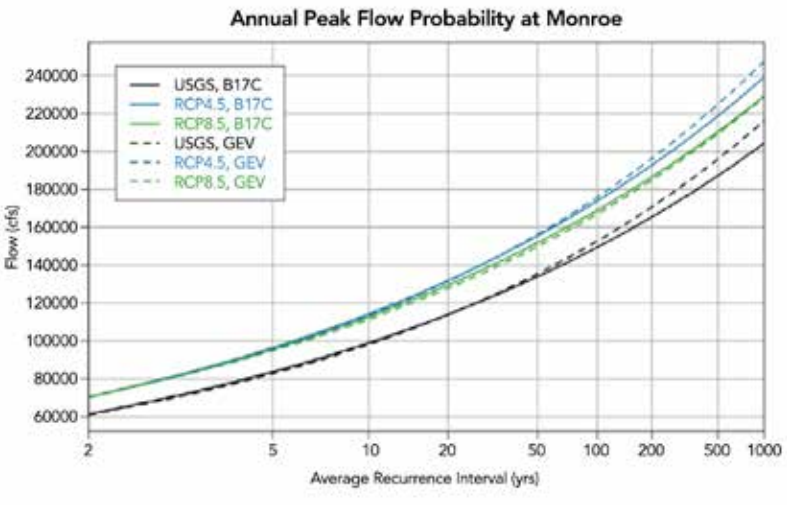
Actionable information and methods for the incorporation of climate science in the resilient design of new critical infrastructure has been non-existent, though increasingly required. In many cases, the infrastructure designed under stationary climate assumptions (e.g., historical 100-year return period) is largely inadequate to handle changes in flood events. To this end, recent policy changes in floodplain management guidelines call for the inclusion of climate-informed science. However, actionable climate information or guidelines for its inclusion at a local scale are not widely available.

The objective of this research is to develop modeling and simulation tools and methodologies to help stakeholders (including policymakers, planners, and engineers) understand vulnerabilities and consequences related to the non-stationarity of precipitation events. This process includes the translation of global, long-term climate projections into local scale, actionable information. These tools will provide a means to develop mitigation and adaptation strategies to ensure resilient designs for critical infrastructure systems.

The focus of this project was developing future frequency distributions of flow rates for the Snohomish River located near Monroe, WA. The Snohomish River watershed was selected as a demonstration region given relative contributions of rain, snow, and rain on snow to potential flooding. In a companion project, these frequency distributions were used to quantify the impact that changes in flood frequency have in flood consequences and risk.

The crux of translation of climate data to local-scale runoff distributions is the simulation of the hydrological processes forced by regional climate data. The distributed hydrology soil vegetation model was used to simulate the complex dynamics of precipitation, infiltration, snow accumulation/melt, and runoff at an hourly time-scale. We calibrated this hydrologic model with a distinct emphasis on capturing extreme runoff events using observations from U.S. Geological Survey stream gages and observed meteorological data from local weather stations and historical data from the North American Land Data Assimilation System. This model was specifically calibrated for high flows to ensure that extreme events are properly accounted for in future time period simulations.

The future hydrologic periods were forced by regional climate model data developed at PNNL. These results included hourly observations of air



Analysis of absorbing organic aerosol produced from the photooxidation of toluene under high-NO_x conditions. Liquid chromatography separation followed by ultraviolet-visible spectroscopy detection and mass spectrometric detection is used to identify specific molecular products responsible for aerosol absorption (browning).

PN15074/2749

temperature, wind speed, relative humidity, incoming short-wave radiation, long-wave radiation, and precipitation at 1/8 degree resolution. We used these meteorological forcings for two scenarios: representative concentration pathway (RCP) 4.5 and 8.5. These data cover a time period from 2005 to 2100.

Two frequency analysis methods were used to characterize the runoff from the simulations- Bulletin 17C and generalized extreme value. Using the frequency distributions, we are able to quantify changes in intensity and frequency of extreme runoff events (including rain, snow, and rain on snow) over future periods and scenarios. For example, RCP 4.5 showed a consistent 15% increase in runoff over all return periods. In addition, a 100-year flood event today is projected to become approximately a 48-year event in the future.

The primary outcome of this project is the demonstration of the ability to utilize regional-scale climate data to develop local-scale runoff distributions that can be used for community and infrastructure planning. While the focus of this project was extreme precipitation and runoff relative to flooding, the same approach can be utilized to investigate water management strategies relative to temporal shifts in annual runoff volume under water stressed conditions.

Nonstationary Climate Considerations - Floods and Consequences

David R. Judi

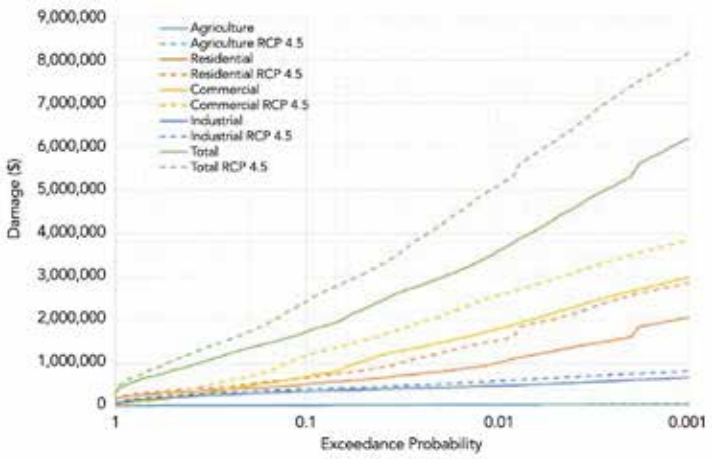
Tools and methodologies for global and regional climate model projections to develop local-scale, actionable information will enhance the resilient design of communities and critical infrastructure under non-stationary conditions.

Flooding has been observed to become more prevalent and is expected to worsen with a changing climate, including potential increased precipitation and snowmelt runoff. For example, some coastal areas frequently experience flooding resulting from relatively minor precipitation and tidal events because of local changes in sea level. Inland areas have also become more vulnerable to flooding. The majority of the United States has seen an increase in short duration, high intensity precipitation events and these events are expected to increase in frequency and intensity. The observed and projected changes in precipitation are commonly referred to as a non-stationary climate.

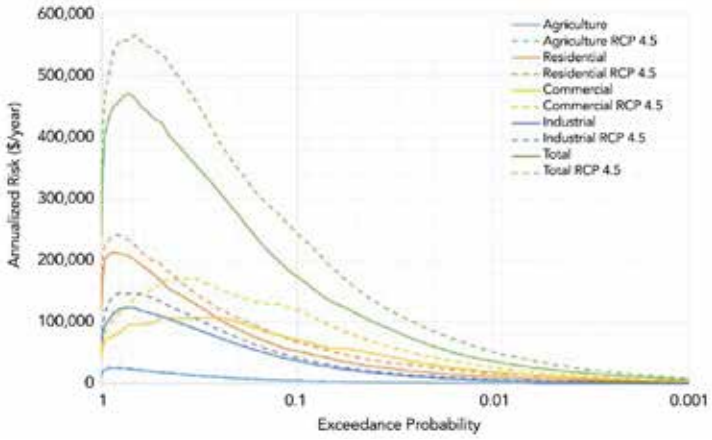
Actionable information and methods for the incorporation of climate science in the resilient design of new critical infrastructure has been non-existent though increasingly required. In many cases, the infrastructure designed under stationary climate assumptions (e.g., historical 100-year return period) is largely inadequate to handle changes in flood events. To this end, recent policy changes in floodplain management guidelines call for the inclusion of climate-informed science. However, actionable climate information or guidelines for its inclusion at a local-scale are not widely available.

The objective of this research is to develop modeling and simulation tools and methodologies to help stakeholders (including policymakers, planners, and engineers) understand vulnerabilities and consequences related to the non-stationarity of precipitation events. This process includes the translation of global, long-term climate projections into local scale, actionable information. These tools will provide a means to develop mitigation and adaptation strategies to ensure resilient designs for critical infrastructure systems.

The focus of this project was using flood frequency distributions of historical and future flow rates to derive estimates of flooding and consequences for the Snohomish River located near Monroe, WA. The Snohomish River watershed was selected as a demonstration region given relative contributions of rain, snow, and rain on snow to potential flooding. In a companion project, these frequency distributions were developed using regional climate model forcings for representative concentration pathway (RCP) 4.5 and 8.5 for up to the year 2100. For comparison, frequency distributions using historic U.S. Geological Survey data were also developed.



Comparison of estimated damage from extreme flooding considering historical and future scenarios.



Comparison of estimated damage from extreme flooding considering historical and future scenarios.

To quantify consequences from flooding, we first developed spatial and temporal distributions of flood depth and velocity. This process was accomplished using modeling and simulation based on the shallow water equations and avail-

PN15072I2747

able topographic data. We used Monte Carlo methods to develop 135 flow forcings for each scenario (historic, RCP 4.5, and RCP 8.5). From each simulation, spatial distributions of peak depth and velocity were developed and stored for use in consequence estimation.

To understand consequences (and relative change therein) from a non-stationary climate, we developed models to represent the built environment, specifically focusing on population at risk (e.g., flood exposure) and potential building damage within the residential, commercial, industrial, and agricultural sectors. These models were constructed using U.S. census data, remotely sensed determinations of percent imperviousness, and county-level parcel data and assessed building valuations. We also developed fragility models, a relationship between damage and flood characteristics, for each sector. For each simulation, the flood hazard, built environment, and fragility were combined to assess population at risk and direct economic impact from structural damage. These results were used to estimate expected annual damage and annualized risk relative to the probability of the event.

The changes in population at risk and direct damage are not linear with changes in flow rate frequency. For example, a 100-year flood flow rate that was estimated to increase by 15% results in a 25% increase in population at risk and a 34% increase in total structural damage. Considering the range of the frequency distribution, the total expected annual damage could increase by 23%, with the highest relative change occurring in the commercial sector. The toolset developed provides the ability to incorporate mitigation and adaptation strategies and quantify the impact these strategies have on minimizing damage and population at risk.

For FY 2016, we intend to incorporate non-stationary conditions in the built environment, such as population dynamics and changes in the built environment.

Numerically Robust Climate Simulation Through Improved Interaction between Model Components

Hui Wan

This project offers new methods for representing the interactions between atmospheric processes in numerical models and developing more robust and reliable tools for understanding and predicting climate change.

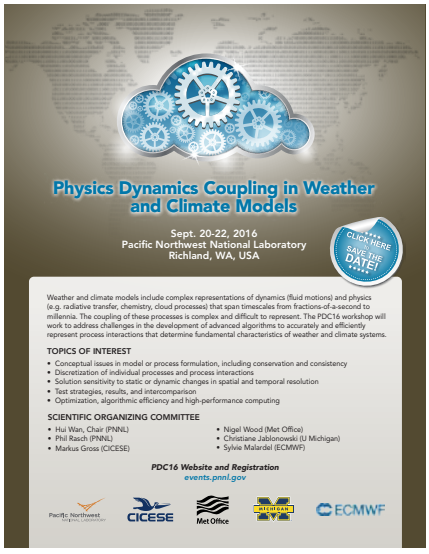
General circulation models (GCMs) that numerically solve the evolution equations of atmospheric motion have been used as a fundamental tool in climate research for more than five decades. Recent progresses in process studies, the fast growth of computing power, and the decision-makers' need for detailed information of regional climate change 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 both with each other and the rest of a model, there is not yet an established theory or standard practice regarding the coupling technique. In contrast, a number of studies have shown disconcerting sensitivities of model behavior to numerical details. The symptoms reveal a major weakness in current climate models, which implies that large structural uncertainties exist in the simulated climate responses to anthropogenic forcing.

The objective of our work is to reduce numerical errors associated with component coupling in climate models. Through the development of new coupling methods, we aim to achieve a higher level of numerical and physical consistency between different processes and constrain artificial sensitivities in climate predictions. In previous years of the project, we used a simple model to demonstrate that the widely used operator splitting technique can cause severe problems when applied to strongly competing or compensating processes. Substantial improvement in numerical accuracy can be achieved by solving multiple processes simultaneously. For the Community Atmosphere Model (CAM) version 5, we performed an atmospheric water budget analysis and found that complex process interactions are ubiquitous in cloud regimes of important climate impact. The analysis also revealed that the process coupling technique currently used in the model leads to artificial sensitivities to model time step in terms of the simulated mean climate and process rates.

Our investigation in the second half of the project focused on pinpointing the source of numerical artifacts in CAM5. A new strategy was developed for the numerical experimentation, which replaces the traditional serial-in-time, multi-year climate integrations by representative ensembles of short simulations that are a few days in length. Validation tests showed that the new method typically helps to reduce the total computational cost by a factor of 15, and the experiment turnaround time by a factor of several hundred, which provides a great potential for efficient use of the leadership computing facilities for numerical experiments that would otherwise be prohibitively expensive. The new strategy was published in and highlighted by the peer-reviewed journal *Geoscientific Model Development*. The computational benefits of the ensemble approach has attracted wide attention in the climate modeling community, and we anticipate that the new technique will have equally wide applications.

Using the ensemble method, numerical simulations were performed to characterize CAM5's time step sensitivity. A time step convergence test was designed and found to be very effective for the quantification of the overall time stepping error and the attribution of such errors to individual model components. This work published in *JAMES: Journal of Advances in Modeling Earth Systems* and was highlighted on the DOE Office of Science homepage.

Outcomes of this project have helped establish the principle investigator's (PI's) and PNNL's reputation as a leader in the area of numerical methods for process coupling in climate models. The PI gave invited oral presentations at two international conferences in FY 2015. In addition, she will serve as chairperson of the Scientific Organizing Committee for the second Physics Dynamic Coupling workshop hosted by PNNL in September 2016.



Flyer from an international workshop the PI is organizing for FY 2016.

PN12059/2460

Quantifying Carbon Fluxes and Underlying Mechanisms Using Multiple Data Sets with a Joint Land-atmosphere Ensemble Kalman Filter Data Assimilation System

Ghassem R. Asrar

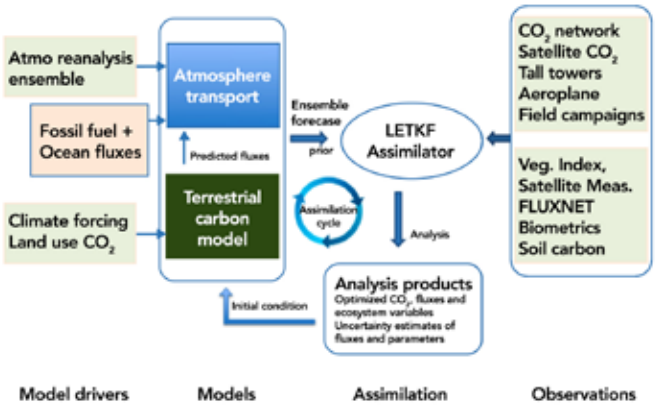
We are using and developing a coupled land-atmosphere carbon data assimilation system that will simultaneously handle multiple modeling components as well as multiple streams of data.

The working hypothesis of this project is that using a combination of measurements in our proposed coupled land-atmosphere data assimilation system will enable us to characterize the spatial and temporal variability, hence the uncertainties associated with major global/regional carbon sources and sinks. To assess these concerns, our developed system will use observations from Orbiting Carbon Observatory-2 and GOSAT satellites with other datasets such as CO_2 measurements from flask sampling network, remotely sensed vegetation indices and fraction of Absorbed Photosynthetically Active Radiation, FLUXNET CO_2, and water and heat flux measurements, vegetation and soil biometrics, and land cover/use history. Scientific knowledge and developed data sets are important for bounding uncertainties associated with climate sensitivity to CO_2 build up in the atmosphere; determining the capacity of terrestrial ecosystems in sequestering excess CO_2 from the atmosphere; and developing climate- and carbon-related policies and management practices for the future.

During FY 2015, we assembled key data sets, including historical remotely sensed observations, and took high resolution photographs for key eddy flux observation sites and major agro-economic zones in the United States. We participated in a project focused on inter-model comparisons to link VEGAS vegetation-atmosphere model with other models for better characterizing uncertainties in simulating the carbon cycle, which is essential for future uncertainty analyses of coupled carbon data assimilation experiments. Specifically for data sets, we completed processing MODIS NDVI forcing data; obtained and conducted initial analysis of FLUXNET data; compared VEGAS model in a forward approach for several sites; obtained and processed historical climate driver data and future scenarios from ISIMIP; and conducted FLUXNET tower footprint analysis using high resolution satellite/aerial images for several sites, including Harvard Forest. For model development, we added a real-time Gregorian calendar to the VEGAS model necessary for assimilating FLUXNET data; completed LETKF-GEOSChem coupling with initial OSSE experiments; and have coupling LETKF-VEGAS in progress.

ISI-MIP consists of two sets of experiments: historical and future. There are four historical experiments primarily based on different climate data. ISI-MIP provides land cover type and land use data based on HYDE3.1 crop land and pasture areas. The ISI-MIP project requires spatial resolution of simulations to be at 0.125 degree. In addition, we ran the VEGAS model at 0.5 and aggregated to 2.5 degrees spatial resolution for further analyses. Based on these simulations, we observed some variation in net primary productivity (NPP) of 7–10% and soil carbon (CSOIL) of 6–8% under different historical climate conditions. We also observed some differences in carbon allocation to plant roots (CROOT), and woody biomass (CWOOD). Other than these variables, we have not seen any appreciable differences among other VEGAS model outputs.

We presented the early results from our research activities as invited talks at the American Geophysical Union meetings and the North American Carbon Project in February 2015. We also presented some of our research results at the Ecological Society of America in September. As a result of this project, articles have been published in the journals *Earth System*



A joint land-atmosphere carbon data assimilation system

PN14082/2666

Dynamics and Ecological Modeling and, as of FY 2015 end, two additional manuscripts are being prepared for publication.

Next, we will focus on the ISI-MIP future scenarios experiments. There are a total of five experiments and 13 different simulations for the major representative concentration pathways (RCPs) of 2.6, 4.5, 6.0, and 8.5 watts per square meter, and corresponding CO_2 concentrations. Other research activities planned for FY 2016 include a series of coupled carbon data assimilation experiments to understand and quantify 1) the complimentary features of CO_2 measurements by different methods; 2) explore the limits to quantifying seasonal, inter-annual and decadal variability in CO_2 exchange between atmosphere and terrestrial ecosystems; and 3) perform coupled CO_2 assimilation experiments to understand and quantify the spatial variability in sources and sinks of CO_2 for major biomes and eco-regions globally. We will also continue to develop indicators of terrestrial ecosystems phenological and eco-physiological changes based on remotely sensed observations for use in vegetation-atmosphere models such as VEGAS. The initial focus of this task has been the United States, but we will test the applicability of our approach for select eco-regions worldwide.

Regional-Scale Measurement and Modeling of Biogenic Organic Fluxes: Bridging the Gap Between Process Studies and Climate Models

Alex B. Guenther

We are transforming chemical emissions measurements that drive climate change and air pollution.

Climate and air quality models that have been used to make policy decisions previously relied on indirect, highly uncertain emissions data. With positive results from our current project, data can now be based on direct, more accurate measurements on relevant regional scales. Specifically, an airborne capability utilizing the PNNL AAF G1 aircraft for measuring regional scale fluxes of chemical species has been developed that provides observations that can inform and constrain climate and air quality models. This approach goes beyond existing capabilities by using a technique that is more accurate and enables emission measurements on much higher spatial scales than previously has been possible. In addition, we are integrating the high spatial resolution and accuracy of aircraft flux measurements with satellite observations to enable global continuous coverage of emission measurements. The approach has been demonstrated using observations from the recent DOE GoAmazon study and he NSF sponsored NOMADSS study and is now available to enhance future aircraft and modeling studies. This capability can now be extended to other important chemical constituents (e.g., aerosols and greenhouse gases) and other sources (e.g., urban and industrial facilities).

The developed approach for calculating and evaluating high spatial resolution aircraft flux measurements was based on the wavelet technique which enables relatively high spatial resolution flux measurements. An approach for integrating aircraft observations with satellite data was also formulated and demonstrated using these field data sets. In addition to the aircraft campaigns, satellite data-derived estimates cover terrestrial ecosystem emissions, canopy coverage, photosynthetic activity, and environmental conditions, including soil moisture, solar radiation, and canopy temperature. An approach for analyzing and comparing satellite data and direct flux measurements was developed to identify the cause of disagreement between "bottom-up" (earth system model) and "top-down" (e.g., satellite atmospheric data derived) emission estimates.

MATLAB software was created to process PNNL G1 aircraft VOC and wind data and to calculate eddy covariance fluxes using the wavelet technique. An approach was also developed to calculate the vertical change in isoprene fluxes (flux divergence) to estimate regional OH concentrations.

During FY 2015, input was provided for flight planning for the DOE-sponsored GoAmazon study to optimize flux measurements from the PNNL G1 aircraft. An assessment of the observations from this study demonstrates the successful application of this technique. Research results indicate that fluxes of most compounds are relatively low and near or below the detection limit. However, emissions of isoprene were successfully estimated using the G1 aircraft observations. Our results of have been published in two separate articles in *Atmospheric Chemistry and Physics* and, as of FY 2015 end, another manuscript is under consideration at another peer-reviewed journal.

Also for FY 2015, the accuracy of the aircraft flux measurements was assessed and shown to be acceptable for model development and evaluation. Discrepancies between direct aircraft measurements, earth system model predictions, and estimates based on satellite atmospheric data were identified, and approaches for reconciling these differenced were formulated. This process will involve examining not only the total fluxes but also investigating the individual components that contribute to the total flux. The observations from the DOE GoAmazon study indicate that there is a substantial difference in the emissions from lowland and upland tropical forests and satellite observations confirm these results. This novel observation was the direct result of the development of this new capability, which is also being used to improve the emission estimates used for DOE climate modeling studies.

PN14039/2623

Simultaneous ^{14}C and T Dating of Environmental Organic Matter

James J. Moran

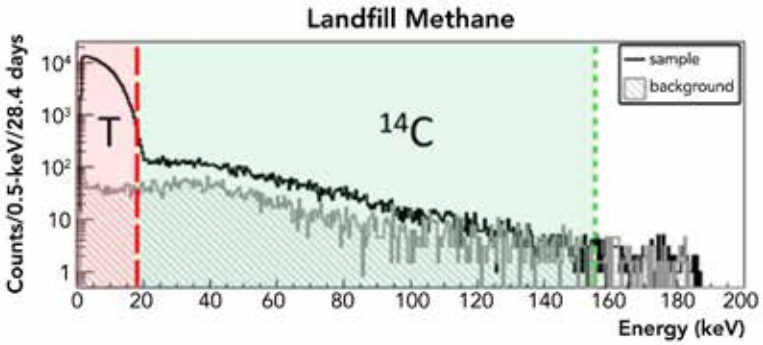
We are developing high sensitivity methods for tritium age dating of organic compounds coupled with other approaches to provide a powerful tool for detailed analysis of carbon (C) cycling through environmental systems.

A well-established method, ^{14}C age dating of organic samples, enables research investigations in areas as varied as microbial substrate tracking, carbon cycling, dating anthropological samples, atmospheric chemistry, and biomarker sourcing. By definition, however, organic molecules also contain hydrogen that can be independently age dated using tritium (T) analysis. Tritium has a much shorter half-life than ^{14}C and can thus be used to track different processes and target different age ranges than ^{14}C. While T has widespread applications in hydrologic, limnologic, oceanographic and other investigations, current measurement approaches make it difficult to apply to organic molecules due to the large sample size requirements for analysis. The primary technological goal of this project is to improve the measurement sensitivity of T such that modest amounts of organic samples can be used for accurate T dating. Once developed, this approach will provide a platform for enhancing understanding of molecular cycling and stability of environmental organic compounds and refine our understanding of chemical recalcitrance with respect to the C cycle.

We will test the applicability of this new capability by characterizing the relative ^{14}C and T ages of soil organic C fractions. Worldwide, soil stores a tremendous amount of carbon, yet key characteristics governing its stability remain undefined. For example, some C fractions appear nominally passive (i.e., abundance does not appear to change) but may actually be quite dynamic. Carbon-14 measurements can offer an understanding of the carbon age stored in these compounds; on its own, it has limited ability for determining stability of these fractions because C could be turned over and incorporated into different organic materials without altering the ^{14}C content. Tritium measurements applied to these organic fractions will provide added resolution into the stability of soil organic carbon and help assess the degree to which this stability is controlled by the molecular structures of the organic fraction versus physical organization of the soil (i.e., proximity to surface or ground waters and the dynamics of those water fluxes). Our approach will allow us to assess compound degradation sensitively at an early stage.

To date, this project has focused on three different technological areas, with successful project conclusion hinging on integration of each of these facets into a complete capability. The major elements being developed include effective conversion of organic samples into methane, developing refined capabilities for and performing isotopic characterization of synthesized methane, and modeling analyte decay within a detector to enhance counting accuracy.

Methane synthesis. Central to the project's success is the ability to convert organic samples into methane which is an ideal gas for dual isotopic measurement by proportional counting. We have developed the hardware needed to combust organic samples and quantitatively collect the resulting product water and CO_2. We are currently constructing the hardware needed to then convert this water and CO_2 into methane. The general approach utilizes a heated zone with zinc or manganese reagent to effectively crack water and trap the byproduct oxygen (immobilized as either a zinc of manganese oxide) resulting in net molecular hydrogen (H_2) production. A heated ruthenium catalyst then catalyzes methane formation from the hydrogen and CO_2. A preliminary system demonstrated effective methane synthesis and a larger volume system is under construction. The larger volume/final system will be integrated with a methane purification line to deliver a



Decay spectrum of landfill-sampled methane gas in an ultra-low background proportional counter. Clearly visible are the T and ^{14}C decay regions that enable dual quantification of both isotopes. There is slight overlap between the T and ^{14}C decay energies, where a portion of the ^{14}C spectra lies under the T region. Efforts are underway to model this overlap to assign decay events properly to each isotope.

PN14068/2652

metered amount of product methane into a proportional counter for isotopic measurement. Significant care is being taken to minimize any potential for carryover between samples. This is especially challenging given the ability of H_2 intermediate to diffuse into steel vessels (with the potential for mixing with subsequent samples). As a result, each of these steps is being performed in a glass reactor and only after initial purification, to remove any unreacted H_2, is the sample gas allowed to contact any metal surfaces.

Isotopic measurement and background determination. Multiple ultra-low-background proportional counters (ULBPCs) were fully characterized for this project using 7-atm background composed of a 90% argon/10% methane (P10) gas blend and measured in PNNL's Shallow Underground Laboratory. These backgrounds will be used in future sample calibration. Work continues on developing the stand-alone hardware needed to precisely fill these counters with a known volume of sample-derived methane and then introduce the proper amount of argon fill gas. To date, this system is constructed and in final validation.

We demonstrated simultaneous ^{14}C and T measurement using samples of environmental methane collected from a landfill and wastewater treatment plant site. Comparison of simultaneous measurements performed at PNNL to individual T and ^{14}C quantification made by a commercial vendor (with much higher sample volumes) demonstrated the dual isotope approach's vastly improved sensitivity (requiring orders of magnitude less sample) with highest precision and accuracy for samples with elevated T, compared to ^{14}C, content.

Modeling of sample dynamics in a proportional counter. Electrical field models have been developed to better understand the internal workings of the proportional counters used as a basis for making T measurements. The electron avalanche replicates detector pulse formation from experimental results and will be used to guide future detector design to further enhance sensitivity gains. The tools developed for simulations in Garfield++ have been thoroughly tested and vetted. Both 2D and 3D Maxwell solutions can be imported for further detector analysis in Garfield++. Recent simulations have been focused on using the simulations to estimate the fiducial volume of the ULBPC. This work has been developed as piecewise: at each step a further restriction is imposed to more closely represent an actual measurement. Enhanced understanding of analyte decays within these detectors enabled by the modeling efforts will directly improve final measurement precision, accuracy, and sensitivity in future sample analyses.

Using Multiple-Degree-of-Freedom Feedback to Auto-Tune Climate Models

Benjamin S. Kravitz

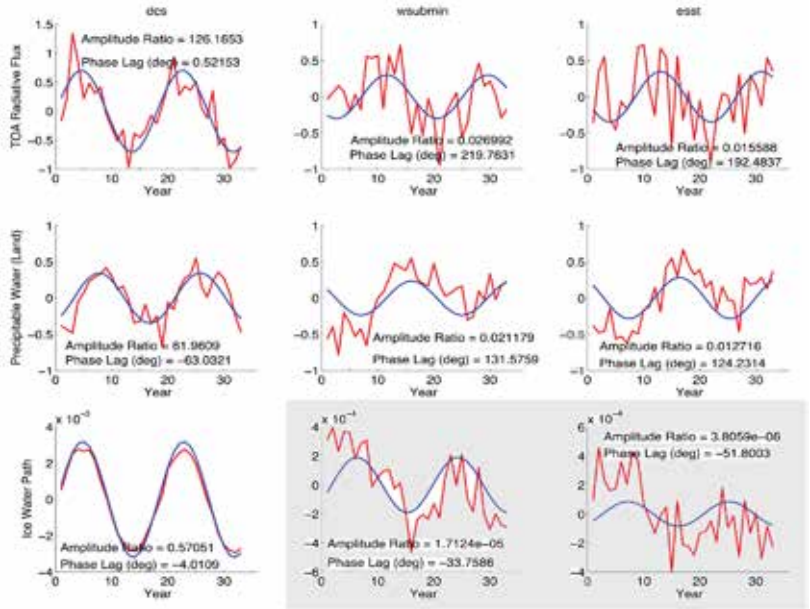
A rigorous, computationally inexpensive method of tuning climate models is introduced to use tools automatically from control theory (feedback).

Climate modeling is one of the pillars of understanding how human activities are changing the earth system. These vastly complex models have a number of parameters that must be tuned (within the realm of physical understanding of the processes involved) so that the models are capable of accurately reproducing observations of past and present climate. Determining the appropriate values of these tuning parameters is a long, expensive process that often requires expert knowledge about the intricacies of the models.

Our objective is to introduce a rigorous, relatively inexpensive method of simultaneously tuning multiple climate parameters using tools from control theory. One of the scientific goals is to understand whether there are multiple plausibly tuned climate states that have different emergent properties. As an example, we will attempt to determine how much of the uncertainty in model projections of future global warming is due to the way climate models are tuned. It is anticipated that our research will help to clarify some of the uncertainties in climate model response to scenarios of future greenhouse gas emissions changes.

During FY 2015, we successfully identified three objectives for climate model tuning based on a survey of the literature regarding common tuning objectives as well as expert elicitation of scientists at PNNL. We also identified three tuning parameters that modify these objectives, such that the influence matrix – the relationships between the inputs and outputs when viewed as a matrix – is triangular. In addition, we successfully completed system identification, wherein magnitude and phase information about the influence matrix is obtained. Specifically, this task is accomplished by inserting a sinusoidal perturbation into the model that modifies each tuning parameter.

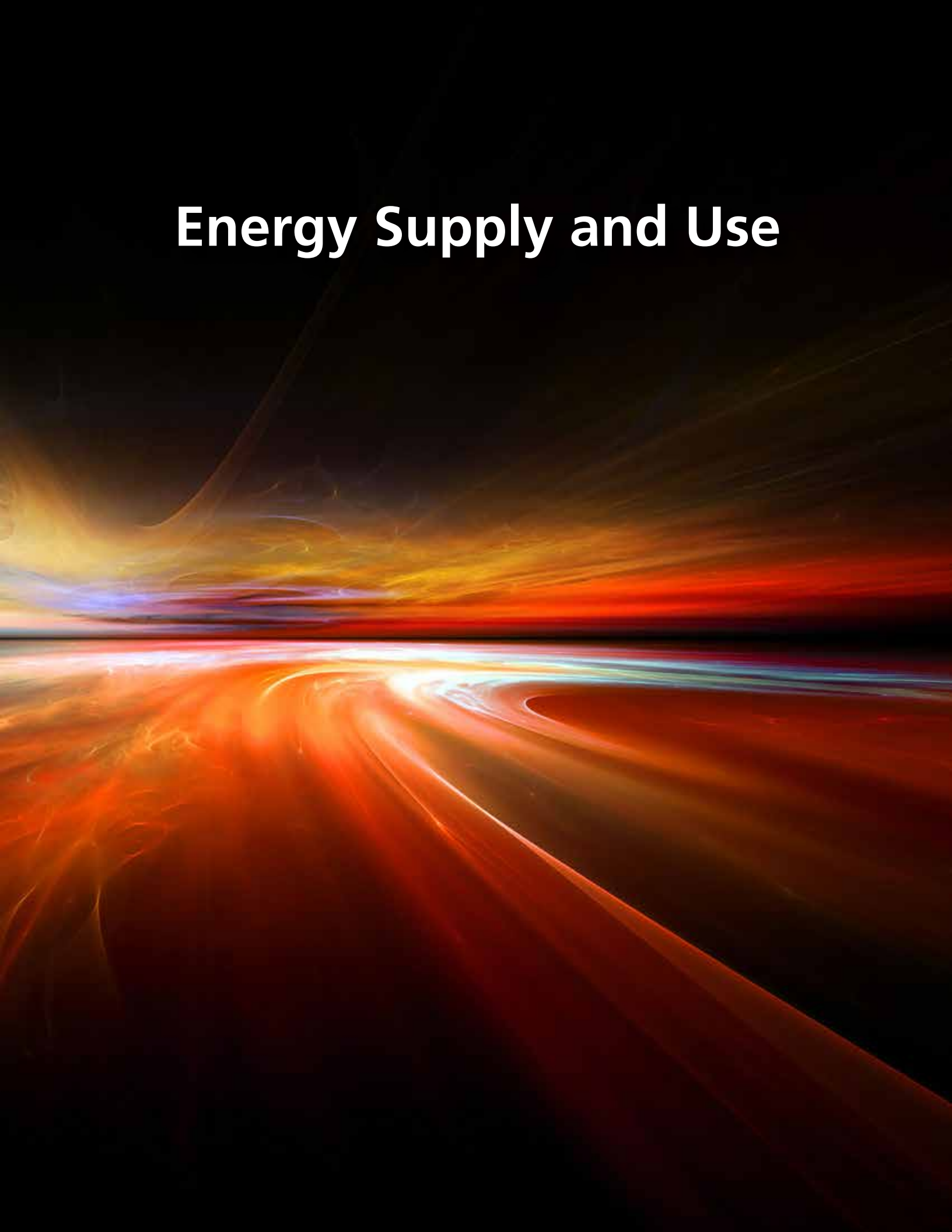
The next stage in FY 2016 will be to design the feedback algorithm using techniques from control theory such that the three tuning parameters are regularly and automatically adjusted such that the objectives are met. After the feedback algorithm is designed, two simulations will be conducted in which the climate is "thrown off" in two different directions, and tuning is used to "bring it back." These two cases will likely result in two different sets of tuning parameters, both of which result in tuned climates. Additionally, these cases will be used to ascertain any differences in emergent properties for the two different sets of tuning parameters. One possible outcome is two differently tuned climates, both of which are plausible, yet have different responses to changes in greenhouse gases or aerosols.



The above images show how the three tuning parameters (columns) affect the three outputs (rows). Actual model responses to input signals (sinusoidal, 18-year period) are in red; best fits are in blue. The text indicates the amplitude ratio (of the output to the input) and phase lag (the shift between input and output signals). Greyed out regions indicate relationships that are not significant enough to affect design of the feedback algorithm. The matrix is upper triangular, indicating that designing a feedback algorithm will be straightforward.

PN15098/2773

Energy Supply and Use



Advanced Visual Analytic for the Power Grid

George Chin, Jr.

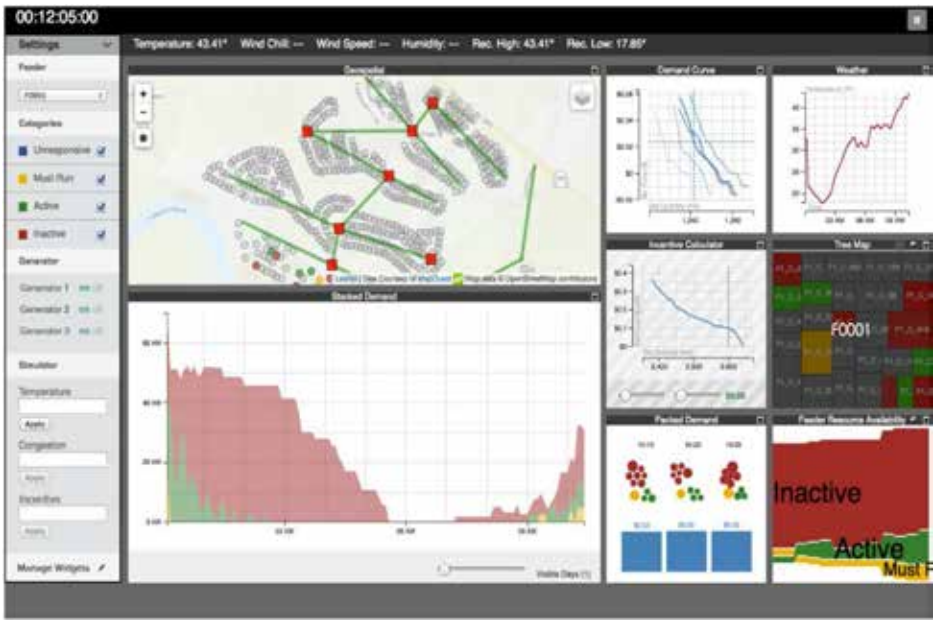
To enable an effective time-critical power grid analysis, interactive visual analytic interfaces that combine complex models and data can provide necessary insights into and understanding of the state and course of an existing or proposed power system.

Developing useful, effective visual analytics tools for the future power grid is a significant challenge. The power grid has three trials of scale: system complexity, big data, and computational requirements. Presenting users with interactive visual analytic interfaces that can manage these three scales while providing an intuitive representation and navigable interactions will be the primary focus of our work. We will build on existing efforts in data management, modeling, and architecture. Developing systems for interactive analysis requires specific design criteria optimal for interactive analysis that is often at odds with storage or computation design. All three have to be accounted for in a way that balances the needs of each, where the goal is to provide planners and operators with visual analytics tools that meet mission needs efficiently.

A prototype visual analytics system for planners to assess future grid configurations for supporting power transmission and distribution in the dramatically changing grid will be created over the next two decades. The work will emphasize adaptable visual interfaces that support deep analysis while leveraging existing modeling as well as simulation and architecture projects. We will demonstrate the value of a holistic view of the future power grid through powerful visual interfaces. Additionally, we will develop and deploy powerful visual steering capabilities that will allow power grid operators and planners to steer models and simulations dynamically in use cases and scenarios that represent the future power grid. As a result, this project will provide an integration demonstration capability for selected modeling and simulation tasks as well as for the GridOPTICS™ framework.

In previous years, in-depth design sessions were conducted with GridOPTICS™ Software System (GOSS) and model developers to derive power grid analysis use cases to serve as target domain problems for a visual steering and modeling environment (VSME). The primary use cases focused on demand-response modeling using the GridLab-D™ distribution system to simulate retail markets at multiple feeders and the MatPower system to simulate wholesale markets. Both GridLab-D™ and MatPower simulations were augmented to provide market models on other projects. Developed demand-response use cases concentrated on distribution system and load service entity (LSE) operators and planners as users. Distribution system users would primarily focus on managing retail market auctions, while LSE users would engage a combination of auctions, incentives, and distributed generation.

To enable use cases, communications among simulated systems are supported and synchronized using the next-generation GridOPTICS™ Framework for Network Co-Simulation (FNCS) streamed into GOSS, where VSME can access the communications stream, model parameters, and results. VSME was implemented as a GOSS application that may publish and subscribe to the GOSS framework. Through GOSS, VSME connects to FNCS to access the synchronized data stream among the simulations using Websockets. The GridLab-D™ and MatPower applications were modified such that VSME may steer those applications through FNCS parameters. Specific transfer mechanisms, protocols, and data formats passed in the communications stream were also elaborated and developed.



The visual steering and modeling environment dashboard.

PN13081/2562

For visual analytics methods and tools, we developed a suite of power grid visualization techniques deemed to have a strong potential to support the visual analysis of dynamic power grid data, relationships, and behaviors. The suite of visualizations allows users to view dynamic power grid data from different perspectives, including spatial, geospatial, temporal, hierarchical, logical, and categorical. They are designed to be easily configurable to different types of power grid data such as loads, bid prices, bid quantities, locational marginal prices, and generator output. Specific visualization tools that have been developed and configured for the use cases include a geospatial map of homes, feeder load display, historical load curves, geospatial tree map, circular view, incentive calculator, forward LMPs display, and feeder resource availability story flow visualization.

A configurable dashboard that organizes a set of visualizations for a particular use case and provides user interface access to simulation and visualization parameters and controls was developed as part of VSME. Through the dashboard, a user may evaluate different scenarios by adjusting model parameters and immediately seeing and comprehending their effects across the set of intuitive visualizations. Simulation parameters exposed through FNCS for the use cases include outside temperature, congestion, and generator shutdowns. The realized VSME system with dashboard and visualizations were presented to an internal PNNL advisory board during a year-end review as part of the integrated demand-response demonstration.

For FY 2015, a variety of new visual analytics techniques and tools were developed under this project, including weather, dynamic bubble/bar, periodic spiral, parallel coordinates, heat map, and starburst visualizations. In addition, the data streaming component of VSME was redesigned to ingest abstract data streams that are independent of the domain or problem space. The individual visualization tools were then updated to collect data from the abstract data stream and thus became readily configurable and adaptable to different types of data from different problems and use cases.

In addition, the project developed a compute server mechanism that allows the separation of compute and visualization rendering code. For certain high-computation visualizations such as the treemap, the browser could bog down on high-resolution data. For such visualizations, the compute code was separated from the rendering code and executed on a compute server with rendering results passed to the associated visualization in the browser. This change drastically improved the computational performance of high-computation visualizations.

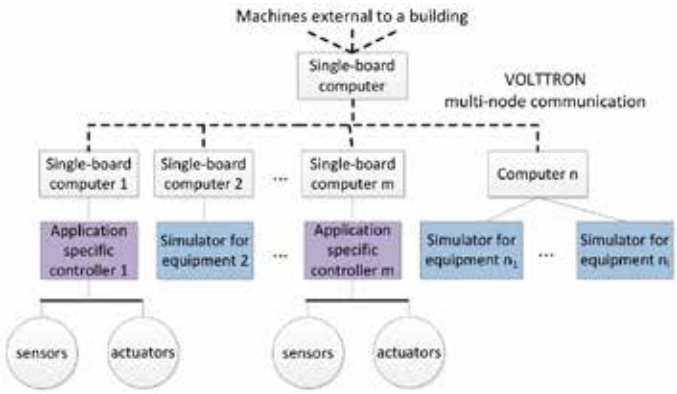
Finally, VSME was extended to support the specification of GridLab-D™ and MatPower models through user interface controls and forms. This approach allows users to interactively define key parameters for the distribution and transmission system models and have those models executed on demand from within VSME.

Agent-Based Testbed for Complex Building Control Systems

Weimin Wang

This project develops a testbed to expedite the application of advanced control theories and tools in buildings for the benefits of energy efficiency, occupant comfort, and reliable operation of the power grid.

Multi-agent systems for distributed controls have been successfully applied to robotic systems, air traffic management, and other uses. However, only minor exploratory studies have been performed thus far for agent-based building controls. Partly from lack of realistic, flexible testbeds for distributed building controls, the limited studies are either ad-hoc simulations or simply tackle simple problems for a specific building. To fill the gap, this project was initiated with the following two major objectives: to develop an agent-based testbed for distributed control of building systems and equipment and for interactions between buildings and the grid; and to demonstrate use of the testbed in investigating agent-based control approaches for representative building systems.



Building testbed structure

We are designing and deploying an advanced building controls testbed in real buildings on PNNL's campus with the following characteristics: 1) it will support interactions among heterogeneous components and systems (e.g., pumps, air-handling units, lighting systems, water heaters, occupant behavior); 2) it can be easily reconfigured to test/validate/demonstrate different control methodologies and tools under realistic but controllable conditions; and 3) it is an integrated part of a larger testbed that includes renewable generation, energy storage, grid, and peer buildings. These characteristics will enable the support of testing and demonstration of new control solutions and technologies developed from other projects.

In FY 2014, we identified testbed requirements from different aspects such as testbed core characteristics and capabilities, data collection, monitoring, communication, experimental setup, and management. Based on these requirements, we proposed the testbed infrastructure. The building tested supports both physical and virtual devices. To achieve distributed controls in real buildings, each application-specific controller is associated with a single-board computer with VOLTTRON™, a PNNL-developed agent execution platform installed, where different control algorithms can be implemented as different agents in the single-board computer. When testing, the applicable control logic implemented in VOLTTRON™ will override the original control logic in the corresponding application-specific controller. The multi-node communication capability of VOLTTRON™ enables a controller to obtain data from related controllers, if necessary. A high-level computer is an interface for communication with external entities. The infrastructure was used at the Building Diagnostics Laboratory (BDL), a test facility on PNNL's campus. A test case on the single-duct variable-air-volume system at BDL was created to test the key VOLTTRON™ functionalities in the testbed.

The testbed infrastructure can support different control topologies, depending on the location of control functionalities. For example, centralized controls are achieved if all single-board computers at the bottom level provide no control capabilities except passing data while the high-level computer has all control functionalities. Similarly, hierarchical controls can be achieved by introducing middle-level single-board computers and allocating control functionalities accordingly.

During FY 2015, the building testbed module infrastructure was enhanced to allow switch between original control systems and new controls. Specifically, the testbed was expanded to include the system engineering building. A number of Modelica models were developed for different building components such as variable-air-volume terminal boxes, air-handling units, chillers, and cooling towers. We implemented a couple of use cases and verified the ability of the initial test bed to support local data storage, data collection at different intervals, remote access and configuration, different control topologies, and communications among heterogeneous devices. We also designed and implemented a solution to hardware-in-loop based on the VOLTTRON™ and Modelica models.

In FY 2016, we will complete the testbed for the Systems Engineering Building on the PNNL campus, supporting both physical components and simulators. In addition, we will initiate a case study using the testbed for distributed building controls.

PN14044/2628

Aggregate Load Modeling and Control for Power Grid Regulation Services

David P. Chassin

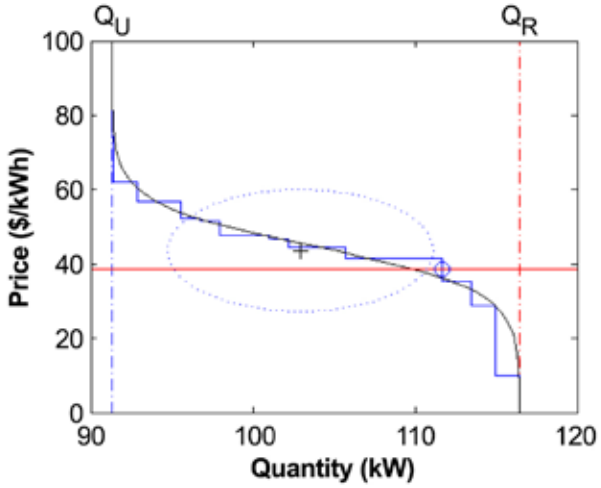
This project is modeling aggregated loads for the design and analysis of distributed control strategies to support demand-based regulation services for the grid.

Modeling controllable load is a vital step toward full integration of renewable resources, where the appropriately chosen and calibrated models will enable bulk-power system controls using demand resources. The aggregate load modeling problem has been a long-standing challenge and remains one of the principal obstacles to scalable, fast-acting demand-based control solutions that use buildings to enhance and support bulk power system planning and operations. This project bridges the gap between the temporal and physical scales of end-use load and aggregate demand control models that has prevented current load control solutions from being included comprehensively in the larger problem of optimizing energy, power, and ramping resources allocation in bulk power systems.

We are following up on prior work done on modeling electric loads in general and demand response in particular. Previous work was based on a variability power spectrum as a function of a set of independent components that can be used to study both generation and load variability. Aggregate load was modeled as though it is composed of underlying models, which could be directly measured or indirectly disaggregated from existing data. The key relevant observation is that when under control, the periodic components of loads have phases that are expected to change based on component behavior in well-defined ways compatible to the mathematical formalisms used in modern control theory.

In FY 2015, we collaborated with the University of Victoria's Electrical Engineering Department following up on the development of the new discrete-time zero-deadband residential thermostat by developing a model of aggregate load control at the utility scale. This linear time-invariant load control model enables utilities to design simple demand response dispatch strategies. The model was demonstrated on a variety of standard controllers to illustrate how it can be used to design load control systems using standard control design techniques. The load control model is considerably simpler that previously developed models and thus more approachable for the average utility engineers who wish to engage load in their control systems in a manner similar to generation. The control design is also readily extended to market-based load control for regulation services.

In collaboration with University of Victoria's Economics Department, PNNL applied a random utility model to determine the short-term elasticity of demand response using data collected from the Pacific Northwest GridWise Testbed's Olympic Peninsula study and the Northeast Columbus GridSmart Demonstration projects. We found that demand response bids in transactive systems could be modeled using a logistic demand curve. Using this function we have devise a simple formula to estimate the short-term demand elasticity of loads participating in transactive control system. We also initiated work with the University of Victoria's Mechanical Engineering Department to develop an interconnection-scale model of transactive control systems to enable the design of market-based demand response control systems for regulation and ancillary services using aggregate load control models.



Random utility model of short-term demand response applied to a single transactive market clearing event in Columbus, OH. Blue stair-step line=true demand bid curve; black line=logistic demand curve fit; dotted ellipse=average and one sigma range for the expected price and quantity; solid red line=clearing price, with the blue circle showing clearing quantity and marginal demand units; dot-dashed blue and red lines=demand response lower and upper limits, respectively.

For FY 2016, we will implement the interconnection-scale model of demand response control in GridLAB-D™ for aggregate load control systems and use the model to demonstrate how utilities can simultaneously provide economically dispatchable energy, capacity, and ramp resources from an aggregation of controllable building loads. We will also implement exemplary market-based control strategies based on this analysis for primary, secondary, and tertiary grid services required by grid operators.

PN14040/2624

Complex Systems Control Testbed

Rick M. Pratt

This project provides an experimental and testing infrastructure in which distributed control methodologies and tools can be validated and verified.

The rapid growth of intermittent and decentralized renewable resource electrical generation, the ongoing addition of dispatchable loads (e.g., hot water heaters, energy storage, electric mobility) to utility portfolios, and smart grid growth has led the electrical transmission, generation, and distribution sectors to research control system methodologies other than centralized or hierarchical control. Distributed control is a new approach that has the potential to meet these rapidly growing requirements. The complex control systems testbed will be a unique capability sought out nationally as a flexible, reconfigurable, and scalable operational capability to evaluate formally distributed control system theories, technologies, and tools. The agent-based testbed will be a cohesive, adaptable infrastructure built initially from existing connections to load and generation resources and then extended by leveraging additional grid resources, including renewable energy technologies and buildings, to offer an environment in which distributed control methodologies and tools can be validated and verified by staff, collaborators, and partners.

In this project, we are focused on developing a reliable, flexible, scalable, and adaptable testbed that enables experimental or virtual evaluations of advanced theoretical methodologies and new technologies by gaining control system access to campus and regional physical infrastructures such as Lab Homes, electric vehicle (EV) charging stations, EMSL photovoltaic array, and energy storage projects using the PNNL-developed agent-based VOLTTRON™ platform for distributed control system development. The testbed and other new capabilities from the theory and tools focus areas of this project will provide DOE with a sound scientific basis for growing its energy programs to develop a controls-based research agenda in the building technologies, renewables integration, electricity infrastructure, and smart plug-in vehicle areas.

Our FY 2015 effort built on FY 2014 accomplishments that included creating the testbed control system requirements document integrating both buildings and grid perspectives with the Lab Homes EV charging stations, the VOLTTRON™ agent-based control platform, and local weather conditions. During this year, communications were established with the CAISO utility market to gain price information; Bonneville Power Administration connectivity, which provided current hydro, wind, and thermal generation data; the PNNL photovoltaic array that now supplies power generation data; control of power and hot water flow available from two 80-gallon water heaters; Lab Home thermostats that are remotely controlled; and Lab Home power data that are remotely available. Initial VOLTTRON™ multi-building communications testing was also performed with the buildings initiative team to share power and other control data.

Additionally during FY 2015, a common hardware and software control platform was designed and deployed, enabling a more scalable solution that can control a wide variety of devices using VOLTTRON™ software agents by developing reusable hardware drivers, hardware agents, software agents, or control agents, as needed. This hardware platform also includes the capabilities needed to enable continued device operation in the event of a communication fault or to transition between experimental mode and normal device operation. As network-based, distributed control systems utilize digital communications between devices can be difficult to troubleshoot in real time, a capability was added to display selected control and system data graphically as needed to troubleshoot device/algorithm operation. This display can be enabled to operate on the common hardware platform.

One FY 2015 task was to evaluate the process needed to move a control algorithm from MATLAB and evaluate its performance using the physical control system. For this effort, a simple MATLAB water heater model was developed, tested, and then moved onto the VOLTTRON™ water heater controller and retested. Significant differences between the model and physical system performance were noted. One difference that was easily corrected was the model's insulation performance.

In FY 2016, our testbed development plans include joint use case demonstrations between the physical testbed team and the buildings control team, integration of the simulation team with the physical testbed, the addition of other new load information, and the addition of other controllable loads. These additional inputs will expand the number of variables available for distributed control system research and algorithm development and testing. A significant effort during FY 2016 will be a requirement to integrate the physical testbed configuration and control with an experimental management system that schedules and coordinates the physical and simulation testbeds.

PN14041/2625

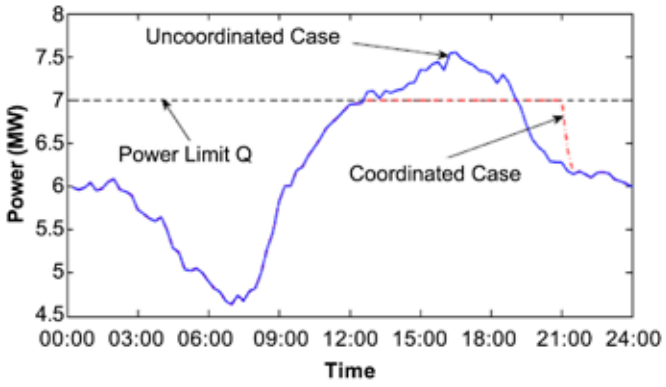
Decision Theory for Incentive Compatible Mechanism Design

Abhishek Somani

The goal of this project is to develop new and analyze existing transactive control mechanisms to enable the coordination of thousands of smart grid assets acting out of self-interest.

Distributed control of a complex system may be viewed as a problem of incentive compatible mechanism design so that the emergent outcomes from actions taken by agents acting out of self-interest are consistent with the overarching control objective. Mechanism design theory (MD), a field of microeconomics study originating from game theory, is a framework for deriving efficient system (or social) outcomes from populations of strategic interacting agents. Normally in game theory, we construct a model of the strategic interaction (the interaction being a "game"), formulate the appropriate agent utility functions, and then solve for equilibria, stable points in which agents choose not to change their strategies. MD is the inverse approach: instead of determining the outcomes from a model of the game, we design the game (i.e., the rules) to reach specific outcomes. Usually, these outcomes maximize (or minimize) some social or system objective function.

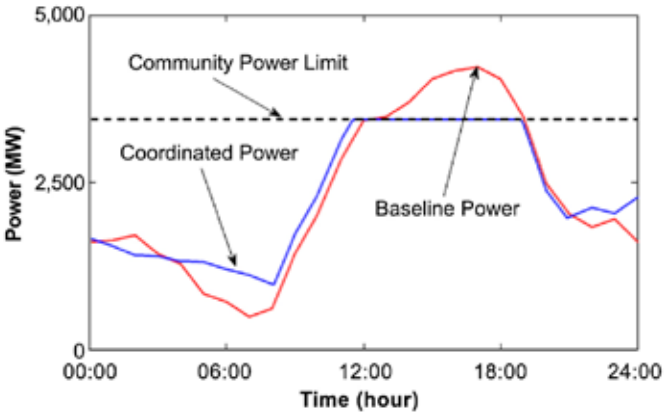
In this project, we will show that large, complex system control can be realized via mechanism design and multi-agent learning. Advancements will be made at the interface of control, mechanism design, and learning.



Aggregate consumption of campus buildings with and without coordination.

We initially used agent-learning methods to derive smart HVAC agents' bidding behavior double auction retail markets, like those used to manage feeder constraints in the recently concluded AEP gridSMART smart grid demonstration project. The bidding strategy in double auction markets is derived without assuming a model for the agents' economic behaviors using a reinforcement learning algorithm. The results for comparing the model-based and -free approaches demonstrated that the model-free bidding strategy gave similar performance to the model-based bidding strategy. Successful representation of economic behavior using model-free approaches will be useful in deploying similar methods for other devices, or a group of devices such as within a building.

The reinforcement learning algorithm can be improved by performing parameter tuning based on certain global evaluation metrics. The algorithm can also be improved by making the reinforcement learning process more sophisticated such as predicting possible impacts of future actions and sensing more information from the environment. Finally, model-free approaches can be applied to represent economic behavior of devices in other market-based mechanisms as well, such as those involving bilateral negotiations to buy and sell energy.



Community consumption profiles with and without aggregation.

Campus/microgrid coordination mechanism. In FY 2014, we proposed a method to coordinate the distribution of electric power/energy within a campus microgrid that employs automated negotiating and bargaining among building agents and that satisfies conditions put forth by both the physical system and semi-cooperative game

PN14045/2629

theory. For FY 2015, we proposed and formulated a cooperative power allocation strategy for a population of commercial buildings within a campus using the theory of Nash bargaining. Dual decomposition technique was used to develop a distributed protocol for commercial buildings to negotiate on sharing a limited power resource. Numerical simulations showed that our allocation strategy was effective to achieve a power allocation for buildings while respecting their own preference and flexibility.

Smart community power coordination mechanism. In FY 2015, we proposed a hierarchical framework for aggregation and coordination of residential flexible loads in a smart community, providing a unified, intuitive tool for the community manager to oversee distributed demand-side resources. We formulated a virtual battery model to represent and aggregate the flexibility of various classes of residential loads such as thermostatically controlled, distributed energy storage, pool pumps, and electric vehicles. We also developed a multi-period Nash-bargaining based power allocation strategy to coordinate the responses of various distributed assets. Unlike the single-period resource allocation method, the multi-period Nash-bargaining approach resulted in "pre-cooling," analogous behavior.

We are currently investigating a multi-period power allocation strategy for commercial buildings, which allows buildings to trade their power capacity rights over a multi-period time horizon. This effort will require modeling of commercial buildings' flexibility over a multi-period time horizon. We are also considering development of a coordination framework that would allow buildings to provide other services, such as fast ramping capacity to facilitate renewable integration, etc., which will require formulating the campus (or community) manager's objective function to include dynamic objectives as opposed to a static one like peak load reduction. These efforts will continue into next year. Overall, our work from FY 2015 yielded two conference presentations and proceedings publications, including IEEE.

In FY 2016, we will work to develop an integrated demonstration of capabilities likely focusing on distributed coordination of resources within a building, which will include responses from deployed physical resources. We have discussed another concept that will combine capabilities developed under other projects to demonstrate a smart city-like concept, coordinating responses from a campus with smart buildings and smart residential communities through a distribution system operator-like entity.

Development of a Combined High-Pressure, High-Temperature NMR Rotor Capability

David W. Hoyt

In situ *tracking of chemical species and reactions at significant temperatures and pressures is critical to understanding the mechanisms involved in future energy solutions such as liquid transportation fuel production from biomass or novel fracturing fluids development for geothermal energy and unconventional oil/gas recovery.*

Magic angle spinning (MAS) nuclear magnetic resonance (NMR) is powerful tool for determining chemical speciation in mixed-phase samples. MAS under combined high temperature and high pressure has never been realized, leaving a large and significant research area unexplored, particularly the ability to monitor *in situ* chemical transformations. To fill this research gap, we are developing the next generation of high pressure MAS-NMR capable of temperatures much higher than currently available. Despite prior work with technology that has had impacted geochemical science with numerous publications, a patent, and subsequent commercial licensing, the design is not capable of the much higher temperatures required for monitoring many catalytic systems under *operando* conditions. To this end, two invention reports (patents underway) have been submitted with the potential to extend the temperature range to as high as 250°C.

Prototypes in a large rotor size (7.5 mm) have been constructed, and initial testing is promising. As smaller rotor size inherently allows for some increase in the pressure limits and higher resolution spectroscopy, translation to 4 mm rotors should increase the limits to 200 bar at 200–250°C. As a stretch goal, a smaller rotor size prototype would be attempted. These new capabilities will make possible a variety of high temperature and high pressure MAS NMR analyses that were previously impossible, including *in situ* MAS NMR analyses of reactions using solid catalysts and material synthesis, hydraulic fracturing fluids system analysis, alternative renewable fuels, bio-oil sample analysis, and core pyrolysis.

An all-ceramic rotor (Approach 1) of 7.5 mm was constructed. Oven testing showed no loss after 1 h at 245°C with steam (~35 atm pressure). In-magnet results with test samples led to a publication in *Chemical Communications*. In addition, commercial rotors with snap-in polymer bushings were constructed in 7.5, 6, and 5 mm sizes. It was found that Torlon (used in previous designs) degraded with the combination of high temperature and steam; therefore, a series of 12 high temperature polymers was explored using a Parr bomb testing apparatus. Some of the advanced materials used for the bushings in Approach 2 rotors are offered as commercial products, with others as research materials. Four materials demonstrated successful showing at 24–30 h in 250°C steam with no degradation effects at this harsh condition, while the remaining eight materials showed a varying tradeoff between brittleness and temperature resistance. Room temperature pressure tests with N_2 gas found that the 7.5 rotors could hold 4000 psi without failure. The 5 mm rotors were tested to 6000 psi (400 bar) in N_2, also without failure. It is expected that the solvent nature of $scCO_2$ may make this limit somewhat lower, but the 5 mm rotors from Approach 2 were tested to 4500 psi (300 bar) with $scCO_2$ with no failure at room temperature.

O-rings were also the main point of failure under the combination of pressure, heat, and steam. Six high temperature chemical-resistant compositions were Parr bomb tested at 250°C with steam; of these, three were selected for tests with rotors. Three 7.5 rotors were tested to 250°C with steam with no loss after 1 h; at 24 h, losses ranged from 20% to 100%. Tests at 200°C showed no loss. These results prompted a nondisclosure agreement with DuPont to explore further other experimental compositions not yet released as commercial products.

The 7.5 and 5 mm rotors with polymer bushing were used on other projects during FY 2015 both internal and external to PNNL:

- Rheoreversible compounds being developed as new fracking proppants were examined using the 5 mm Approach 2 rotors at 110°C and 4000 psi (275 bar) CO_2 for 48 h. Earlier results from 150°C and 120 bar $scCO_2$ using the 7.5 mm rotors resulted in a publication in *Green Chemistry*. It is expected the latest designs/materials will achieve the 200°C and 250 bar requirements to be compatible with the next phase of the project in FY 2016.

PN15053/2728

- A team at the University of California, Santa Barbara used these new rotor designs for an in-depth study to be submitted to the journal *Science*. The ionic liquids and H_2O solutions were either ionic liquid- or H_2O-rich. Observations required a leak-free system and MAS speeds of 5 kHz minimum. The new 5 mm Approach 2 rotors accomplished the zero mass loss requirements at these conditions. The ability to make these observations would not have been possible without the improved designs from this project.
- The 5 mm rotors were used in recent clay-natural organic matter studies at a collaboration of Michigan State-Alfred universities. The new designs were easier to pack and more reliable than with earlier rotors prior to this project. This situation also allowed double the MAS spinning speeds of past work.
- At PNNL, a bio-oil upgrading was investigated at 140°C and 1200 psi pressure. The reaction was followed with both H_2 and N_2 (as an inert blank) with and without the ruthenium-based solid catalyst.

Goals were largely realized for temperature limits increased for the HP/HT technologies for both Approaches 1 and 2. Higher pressure limits were reached using the new 5 mm rotor size of Approach 2, but the most optimal materials for HT have not been fully tested. The most recently identified bushings/o-ring material combinations were being machined at the close of FY 2015. Full testing for the 5 mm rotor system for Approach 2 would establish the maximal combined HT/HP limits if we had another 3–4 months. Further prototype designs for the most common NMR rotor sizes 4 mm and 3.2 mm have been drawn based on the concepts learned over the past year of this project. Future development would allow this technology to be most commercially marketable if these designs were realized in the future.

Distributed Control of Large-Scale Complex Systems

Jianming Lian

We are creating a future distributed control paradigm in electricity infrastructure and building technology to establish the theoretical foundation for transactive control in grid and building to enable the distributed optimal control of smart grid assets for demand response.

Modern systems such as electric power systems and building systems are becoming more interconnected, and complex. In contrast to centralized control, distributed control is emerging as a promising paradigm for the control of large-scale interconnected systems. Although there has been significant progress in distributed control theory for large-scale complex systems, the existing theoretical results cannot be applied to the domains of grid and building due to the ignorance of practical system properties that are specific to application areas in grid and buildings.

In FY 2014, we developed a market-based control framework to coordinate a group of autonomous responsive loads to achieve system-level objectives with price incentives. This framework had the structure of hierarchical decentralized control consisting of the supervisory and the device layers. At the beginning of each market cycle, the coordinator collected the bidding information from each responsive load and determined the clearing price, which was used by each responsive load to determine local control inputs independently.

For FY 2015, we applied a market-based coordination strategy for multi-zone commercial buildings to provide ancillary services. The massive power consumption and enormous thermal storage enable commercial buildings as a great flexible resource for providing ancillary services, which are necessary to enable deep penetration of renewable energy. There were two central problems to be first resolved to enable commercial buildings for participating in the ancillary service market. The first was how to characterize the power flexibility of a multi-zone commercial building, and the second was how to control its power consumption so that it can follow a dispatch power signal while respecting the preference and comfort of individual zones.

We first proposed a scalable, distributed flexibility characterization method for multi-zone commercial buildings and a fair, efficient bargain-based airflow allocation strategy to respect the preference and flexibility of each zone. We studied an agent-based approach to model multi-zone commercial buildings in which each zone was modeled as an agent and contained design-distributed coordination protocols to enable local interaction and negotiation while achieving a global objective. There are many benefits of modeling a commercial building as a multi-agent-system: 1) zonal dynamics are easy to develop and calibrate; 2) the system is flexible, modular, and scalable, whereby the method can be easily applied to heterogeneous buildings; 3) it allows each zone to be more adaptive to structure change, external disturbances, and setting adjustment; 4) compared to centralized flexibility characterization approaches, our approach relied on each zone characterizing its own flexibility based on local information, thus minimizing modeling and computational complexities.

We next proposed a Nash-bargaining-based cooperative airflow allocation strategy for multi-zone commercial buildings. The Nash bargaining solution (NBS) is an attractive approach for solving cooperative resource allocation problems as it balances fairness and efficiency. Unlike non-cooperative game-theoretic approaches in which agents make decisions independently and selfishly, NBS is a unique and pareto-efficient solution that enables agents to make decisions collaboratively to maximize the social welfare. Moreover, using dual decomposition, a distributed bargaining protocol is developed for individual zones to reach the optimal airflow allocation cooperatively while respecting the preference and flexibility of each zone.

Also in FY 2015, we developed a hierarchical control framework for distributed energy resources (DER) coordination. In this framework, we incorporate thermostatically controlled loads (TCLs) into DER coordination, considering the dynamics of an individual TCL device. The proposed framework consists of two layers: on the top, TCL groups are coordinated with other DERs in a distributed manner. On the bottom layer, TCLs within each group are controlled to provide the desired output collectively. The proposed coordination and control strategy combines both economic and control techniques in the sense that it captures both the underlying economics synthetically as well as the detailed dynamics in device level control.

In FY 2016, we will develop the fully dynamic market-based coordination framework with multiple periods and extending the results to energy storage devices and deferrable loads such as plug-in electric vehicles, washers, and dryers. In addition, we will provide use cases to for supporting tool development. In particular, we will provide models and controllers for tool testing, data for the visual analytics platform, and base case for uncertainty quantification, respectively, in the applicable sub-projects.

PN14042/2626

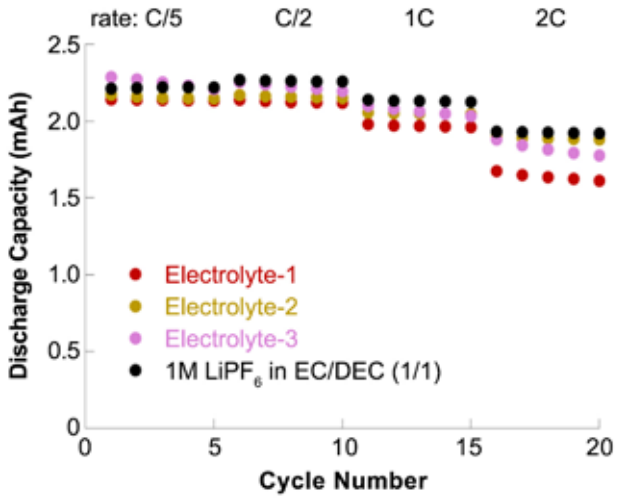
Electrolytes Enabling Low Temperature Battery Operation

Wesley A. Henderson

This project is developing electrolytes to improve battery performance at low temperature that will assist Li-ion applications, thus conserving fuel and greatly reducing vehicle emissions.

Commercial Li-ion batteries are high rate, high capacity cells at room temperature, but these characteristics plummet at low temperatures (< 0°C). Through this project, we will rectify this performance degradation, thereby facilitating the use of Li-ion batteries for diverse applications impacted by low-temperature performance. Our objective is to develop new electrolytes (solvent-salt mixtures) for improved battery performance to enable promising Li-ion applications such as start-stop batteries for micro-hybrid vehicles, conserving fuel and reducing emissions when applied to all new conventional internal combustion engine vehicles.

State-of-the-art Li-ion batteries almost universally contain electrolytes based on the salt $LiPF_6$ and a mixture of carbonate solvents: ethylene carbonate (EC) and an acyclic solvent such as diethyl carbonate (DEC). Although providing excellent performance at ambient temperature, these electrolytes result in poor performance at low temperature with a significant decrease in capacity (e.g., from 100% at 25°C to < 50% at –20°C) and power in large part due to the increasingly sluggish Li+ cation transport within the electrolyte as the temperature is decreased. Batteries with specially tailored electrolytes (e.g., mixing other solvents such as γ-butyrolactone [GBL], ethyl butyrate, or ethyl acetate with carbonate solvents) have improved low temperature performance to –40°C but generally only at significantly reduced discharge rates. We are scrutinizing electrolytes based on unconventional solvents to achieve a cell cycling performance at room temperature comparable to that currently obtained from commercial batteries, but also with an exceptional capacity and rate performance down to –40°C with extensive cycle life.



LTO-LFP coin cell cycling performance with representative new electrolytes and a typical state-of-the-art electrolyte (i.e., 1 M $LiPF_6$ in EC/DEC) cycled at 25°C at different rates (e.g., full capacity discharge time: C/2=2 h, 2C=30 min, etc.).

This project was initiated late in FY 2015. Equipment and instrumentation necessary for this effort was purchased, including two environmental chambers (temperature control –75°C to 200°C), a high precision balance, and battery cyclers capable of testing 80 cells dedicated to the environmental chambers. This equipment/instrumentation was delivered at the very end of FY 2015, so electrolyte testing was initiated using existing available equipment at ambient temperature (25°C).

A large number of electrolyte formulations utilizing the solvent classes proposed for the project and their mixtures were prepared which incorporate a range of lithium salts at different compositions. These substances were initially evaluated by storing them for 1 week at –40°C to ensure that no solvent or solvate crystallization (solidification) occurred, as is common for state-of-the-art electrolytes with carbonate solvents. For the coin cells, tapes of the anode (lithium titanate, or LTO-based) and cathode (lithium iron phosphate, or LFP-based) were cast on large current collector sheets from which the coin cell electrodes were cut using the new dry room/pouch cell fabrication facility (Advanced Battery Facility) equipment at PNNL. This practice ensures that comparisons of cell performance emphasize the electrolyte characteristics rather than the variability in other cell components.

Initial ambient temperature testing of LTO-LFP coin cells with the electrolytes demonstrated that many of the new electrolytes do enable cell cycling commensurate with that of state-of-the-art electrolytes such as 1M $LiPF_6$ in EC/DEC (1/1). Preliminary work has indicated that some of the tested electrolytes do cycle well with LTO electrodes at temperatures as low as –40°C, but the performance in full LTO-LFP cells is not yet known.

Work during FY 2016 will begin utilizing the new acquired battery cyclers and environmental chambers to verify the data reproducibility and commence the accumulation of a compendium of performance data for the cells cycled at low temperatures (i.e., 25°C, 0°C, –20°C, and –40°C), which will allow the validation of the key concepts which have inspired the new electrolyte development for this project.

PN15088/2763

Experimental Management for Controls of Complex Systems Test Bed

Mark J. Rice

Through the creation of this project's test bed, we are reducing researcher experimental overhead and improving the overall experiment process so that additional time and energy can be focused on the research while simultaneously delivering a more concrete product.

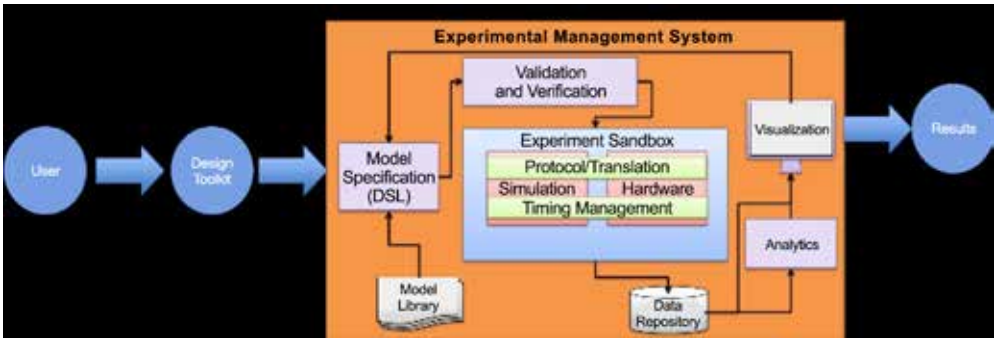
In complex systems, development and deployment of large-scale physical and virtual experiments may encompass the description and configuration of up to millions of devices. Researchers often devote significant time and project resources to experimental setup. A core element of our project is a powerful, flexible test bed that enables researchers who have developed new control schemes to examine performance and behavior in an experimental environment to capture the macroscopic behavior of increasingly complex interacting systems with an adequate degree of fidelity.

The experiment management system (XMS) is designed to provide functions such as experimental design assistance and automation, instrumentation guidance, data collection and curation, model cataloging and sharing, and experiment execution. XMS will manage experiments performed in the test bed, and visual analytics capabilities and graphical interfaces will support the management and monitoring of the test bed setup, experiment orchestration, instrumentation, and data analysis. We are defining the requirements and specification needed to allow tools to be integrated into the test bed and experiments to be run to test and validate control theory and methods developed. The XMS will be built in a way that allows changes in modules (e.g., simulators) to be implemented without the need for updates to other modules.

In FY 2015, we built the framework to deploy control system experiments using multiple simulators from a web portal. The project used OpenStack, a cloud computing management platform, to enable the deployment of multiple computers into an isolated network, a tenant, to perform experiments with. The platform allows XMS to replicate an experimental setup for other research to study start with the same infrastructure. Within XMS, we built virtual machines containing the common simulation software, including GridLAB-D™ (an electrical distribution system simulator), ns-3 (a communication simulator), matpower (a wholesale market simulator), and framework for network co-simulators (FNCS), a PNNL-developed software that enables multiple independent simulators to work in in coordinated manner. Using these images of the simulator Arion, a related project that is developing a domain-specific language, we deployed a demonstration experiment to showcase the XMS and other tools for an annual review. The experimental setup included multiple GridLAB-D™ virtual machines, an ns-3 virtual machine, and FNCS virtual machine. This demonstration showed that we can create the environment (tenant) in <10 min to perform the experiment.

In preparation for next year's work, we have been engaging the agent-based distributed buildings controls and laboratory homes controls project to work on interfacing the XMS with the capabilities built by the projects at the business process, communication/networking, and application levels to ensure integration of the three projects into the test bed. We have begun standing up PNNL agent platform VOLTTRON™ virtual machines in both the XMS and central sever to interact with VOLTTRON™ installations used as part of the test bed. The goal of the central server is to deploy new agents that are different control schemes to VOLTTRON™ installations at laboratory homes and for building a control laboratory. In addition, we created a repository for the data collected during experiment and experiment descriptions hosted in the XMS and provided as a service to other projects that would like to mine collected data.

In FY 2016, we will continue to add features and work with control researchers to perform experiments using the XMS as portal into the test bed. New features to the XMS for FY 2016 include development of method for storing data from experiments, creation of a framework of how different objects will communicate with each other, and the use of the XMS to deploy an experiment on a combined system that includes both physical hardware (hardware-in-loop) and large-scale simulations completed.



The workflow of performing an experiment in the test bed

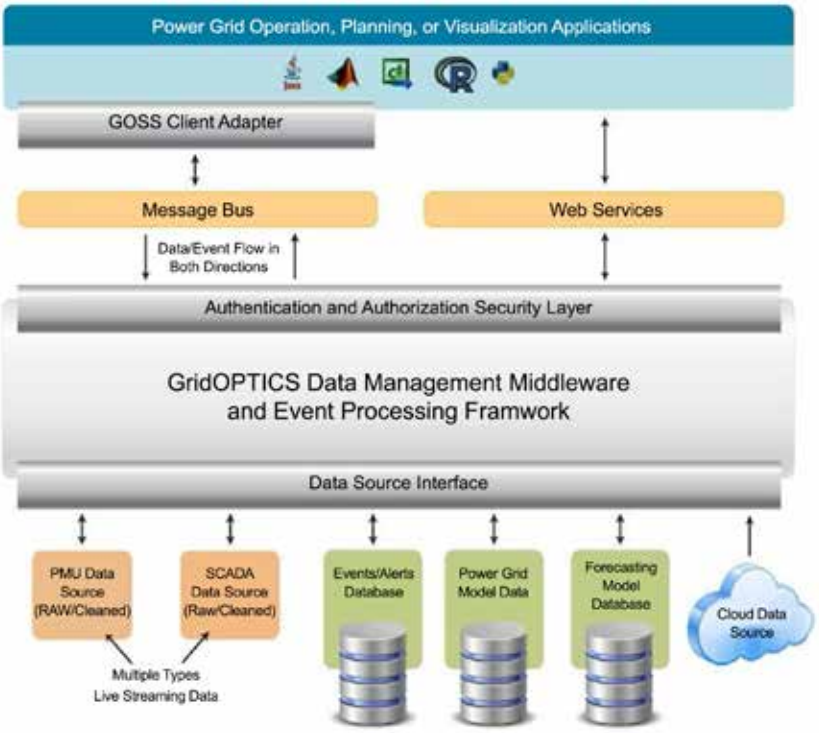
PN15001/2676

GridOPTICS

Poorva Sharma

The GridOPTICS™ software system (GOSS) facilitates the creation of new, modular, and flexible operational and planning platforms that can meet the challenges of the next generation power grid.

The U.S. power system is evolving at a rapid pace. New intermittent distributed power generation and storage technologies, new control paradigms, and new higher fidelity sources of monitoring system state such as phasor measurement units (PMUs) are being deployed. These collective advances are causing the power system to become more dynamic and have more uncertainty. Computational analysis of the power grid for operational and planning purposes needs to evolve to match this emerging dynamic behavior. In turn, software tools available for power grid analysis were developed under a traditional, sequential, workstation-based software paradigm locked into existing vendor software systems for energy and distribution management. This scenario makes it difficult to infuse novel, emerging analysis and data management techniques into power system operations to meet growing computational and big data needs.



GridOPTICS™ software system (GOSS) architecture

The GOSS project is developing a flexible, scalable software architecture that engenders innovation in power grid analytics and data access. Through a set of open application programming interfaces and a robust, high performance and extensible implementation, we are creating a framework in which new and novel data management, analysis, and user-facing technologies can be integrated easily. Primary achievements for GOSS include integrating a range of data collection, analysis, simulation, and visualization technologies to support the operations and planning of the future power grid; providing a framework for integrating novel operations and planning technologies with external power grid systems, including energy and distribution management systems developed by software vendors; providing a client software interface to the GridPACK numerical library; and creating an interface to launch and collect data from high-performance computing applications.

In FY 2013, we developed a GOSS prototype that supports the requirements of high frequency data access and upload from operational, planning, and visual analytics tools running on platforms from Windows workstations to high performance computers. For FY 2014, we continued to integrate with additional applications such as the framework for network co-simulation, operation and planning fusion, and web-based visual analytics. The GOSS framework was updated to be deployed as an OSGI component using Apache Karaf, which allows developers to deploy, install, or add new features to the framework easily and simply for adding a new data source or integrating a new application.

During FY 2015, we added a capability to integrate applications developed in C++ to communicate via GOSS. We assimilated with GridPACK, which was written in C++, to allow the application to send results to a web-based user interface and show better than real-time performance. We also worked with a related project to create a web-based transmission tool that accesses data using the GOSS application program interface

PN13016/2497

(API). Another capability added this year was model conversion from node breaker to bus branch and vice versa, which leverages and expands the GOSS framework. This procedure allows applications to send real-time operating conditions to planning tools and then provides updated near-term planning results to the operators.

In addition to the new capabilities added in FY 2015, we improved on the GOSS security plugin and implemented authentication and authorization to all integrated projects. The GOSS core API was updated to allow for ease-of-integration and fast development for which we specifically used Apache Felix as a framework for easy deployment. We worked on creating a prototype data repository and time series data creation for power grid data, added REST-based web services to the GOSS API, and created a web client for data repository. These efforts allow users to upload, view, edit, and share power grid models. They help maintain model provenance for easy trace-back and allow time series creation for the model based on selected load profile and events.

Before project close, we gave a number of presentations and demonstrations to promote the GOSS framework. An introductory video was shot and shared on PNNL's website and Facebook page to promote the framework to interested possible future partners. An invited presentation about GOSS security features was given at an IEEE international conference, and we spoke at an NASPI work group meeting. Throughout the year, we held a number of meeting presentations and demonstrations for utilities and vendors, from which we received external funding for potentially up to another 3 years.

Human Factors Issues for Lighting Systems

Robert G. Davis

We are preparing standardized tools for human factors assessments of energy efficient lighting systems.

Successful adoption and implementation of energy-efficient lighting technologies depend critically on understanding the effects of buildings systems, including lighting, on human comfort, health, and overall well-being. In many cases, deeper energy savings may result from effectively addressing these human factors issues. A holistic view of sustainable buildings extends beyond energy conservation measures and environmental impact assessments to address the effect of buildings on human comfort, health, and overall well-being. This approach also includes understanding the attitudes and behaviors that can help or hinder the adoption of new technologies. To the above ends, this project initiated new research by studying human responses to lighting, broadening the focus and reputation of the PNNL Advanced Lighting Team. We studied new metrics and techniques for characterizing both the lighting stimulus and human response, and we applied the underlying method to an important new area of research: color quality of lighting.

The most significant technical accomplishment from this project was the planning, completion, and analysis of a human factors experiment that investigated human responses to different lighting conditions. The lighting conditions studied used spectrally tunable lighting fixtures to vary the color quality of the resulting lighting. Specifically, we varied the color quality in terms of two new color metrics recently approved by the Illuminating Engineering Society (IES) that are mathematical constructs based on the spectral power distribution characteristics of light sources and spectral reflectance characteristics of colored objects. There is no explicit guidance on which combinations of values are preferred by building occupants for various applications or purposes, so the experiment conducted for this project represents a starting point for this type of research.

The immersive room in which subjects made judgements about the color quality of the lighting. One of the spectrally tunable lighting fixtures used is seen in the upper left portion of the image.

In our experiment, 28 participants came individually or with one other person to view a specially constructed room with a variety of colored objects that were specifically chosen to represent various hues evenly. During the experimental session, participants viewed the room under 26 different lighting conditions, completing a brief response form for each to indicate their judgments of color quality. Data analysis from the experiment is ongoing and focuses on gaining a better understanding of how participant responses changed for different levels of the new IES metrics. One of the metrics, Rf, relates to the fidelity with which a lighting source renders colors relative to a standard reference light source, while another metric (Rg) relates to the degree to which the lighting source saturates (makes vivid) or desaturates colors relative to the reference source. Preliminary analysis shows that the participants preferred a light source that increased color saturation, especially red; however, preference decreases if the saturation is too great. These aspects of color quality are critical for today's lighting systems, with LED sources becoming more common and LED technology providing opportunities to tune the spectrum of light to an extent not possible with traditional lighting systems. The long-term acceptance of LEDs may depend on manufacturers successfully applying results from human factors experiments such as the one conducted for this project.

In addition to the color quality experiment, our team initiated other efforts related to characterizing the visual stimulus and human responses to lighting systems. For example, we began an investigation into the use of high dynamic range imaging (HDRI) techniques as a means for documenting the stimulus provided by lighting. Visual response to lighting is based on the luminance in lighting

PN15035/2710

patterns in a space, but conventional methods for measuring luminance can be labor intense and impractical in many field situations. HDRI provides opportunities for collecting luminance data quickly and inexpensively but also raises questions about measurement calibration and accuracy. After a review of relevant literature, we tested a new calibration method being developed at the University of Colorado at Boulder and established a collaborative project with its faculty for further work in HDRI.

For documenting human response to lighting, online survey tools have become increasingly important, and our team completed background research into these tools as part of this project. We immediately applied this concept to several related efforts, in one case developing an online questionnaire for gathering reactions to hospital lighting systems from nurses working at different Legacy Health hospitals in Portland, OR. In another example, we are developed a questionnaire for eventual submittal to gather feedback from pilots at Philadelphia International Airport about the glare from airport lighting systems. We will continue to refine our methodologies in this area, evaluating different data collection and analysis tools, and transition this work into our regular research plans with our DOE sponsor.

Our work in this area led to a poster presentation at an annual conference (and subsequently published in the conference proceedings), and another solid-state lighting (SSL)-related manuscript is being prepared (as of FY 2015 end) for journal submission. Perhaps the best measure of the relevance was the broadening of the scope of effort included in the PNNL response to a DOE Lab Call for the funding of SSL research. The successful PNNL proposal included such human factors topics as color quality, metrics for glare assessment, beam quality of directional LED lamps, and user interface issues for advanced controls, among others. These topics are now included in the FY 2016–18 plans for the DOE SSL program funded at PNNL. Although the initial scope of the effort was limited to lighting, we believe that the approach is scalable to address other aspects of the built environment and related human responses, ultimately enabling the assessment of the complete thermal, luminous, and acoustic environment in buildings.

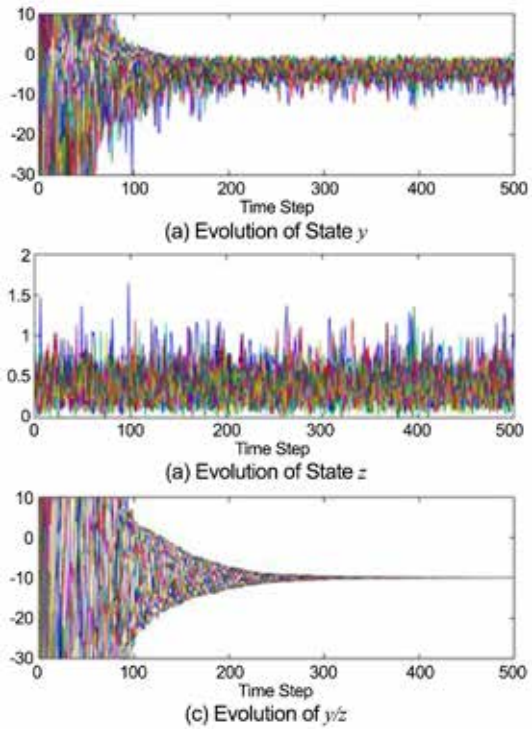
Impacts of Communication Network on Distributed Control

Di Wu

We are studying the effects of communication network on distributed control where system components are not physically co-located and information needs to be exchanged through imperfect communication channels.

Studies devoted to investigating communication network effects in control occur mainly in two categories: networked control system (NCS) and multi-agent coordination (MAC). Many NCS studies are dedicated to estimation within lossy networks, stability analysis, and controller synthesis but primarily consider centralized control schemes. Thus, little attention has been paid to network effects on distributed control. MAC studies focus on control of different agents for achieving a desired coordination in a centralized or distributed manner such as consensus, formation control, task assignment, and estimation. However, in many engineering applications, effective distributed control algorithms are required to allocate resources properly autonomously and optimally.

As communication network behavior impacts are crucial to distributed control, network effects such as time delay and packet dropout can degrade the performance of control systems designed without considering these effects and even fail control and coordination algorithms. As such, the objective of this project is to evaluate network effects in distributed control systems and suggest control protocols that can best accommodate various network effects. In addition, a great effort will go toward improving the control problem formulation to represent building and grid system characteristics and constraints more comprehensively.



Ratio consensus for distributed load shedding using communication networks with time-varying delays.

In FY 2014, we reviewed literature of distributed control for building and grid applications. We studied communication network effects such as time delay, packet drops, and asynchronous effects on different control algorithms and found that these communications may affect algorithm performance and cause non-converging algorithms. Our proof shows that errors in received information may also fail control algorithms. We additionally examined the control and optimization problem formulation based on which the control algorithms are developed.

During FY 2015, we wrote a paper to report our findings on the potential negative impacts of various time delays/packet drops on distributed control algorithms for grid applications. We examined a distributed algorithm for power system economic dispatch problem over directed communication networks with various types of communication time delays. It is found that time delays may result in several negative impacts, including slower convergence rate, convergence to incorrect value, and even divergence. We presented the paper at an IEEE meeting.

To handle more effectively the communication network effects, we proposed a ratio consensus in FY 2015 that was based on a distributed algorithm, where each agent maintains two internal states and updates their values only using the information receiving from neighbors. The proposed algorithm can address various communication time delays and packet drops. Another advantage is that the proposed algorithm can also be used for directed communication networks, in addition to undirected networks. We applied the algorithm to discover the average system overload in distributed load shedding. In particular, in the case of time varying delay, even though both internal states fail to converge, their ratio still converges to the correct average system overload. We submitted a conference paper to report this work.

PN14047/2631

Additionally in FY 2015, we developed minimum time consensus-based distributed algorithms for load shedding and economic dispatch problems. The proposed algorithms are capable of solving problems in a minimum number of time steps rather than asymptotically as in most existing studies. The algorithm relies on existing consensus control protocols but is capable of computing the exact consensus value using each agent's local states over a few time steps before consensus is achieved within reasonable accuracy. As a result, the algorithm accelerates the convergence speed and alleviates the communication burden. The techniques developed here can also be applied to other power system applications such as load restoration and plug-in electric vehicle charging coordination. As of the end of FY 2015, we submitted a manuscript based on this work to a journal for potential publication.

Finally, we developed and tested hierarchical control method for distributed energy resource (DER) coordination. In this work, we proposed a hierarchical control framework to incorporate thermostatically controlled loads (TCLs) into distributed DER coordination that considers the dynamics of individual TCL device. The proposed framework involves two layers. On the top layer, TCL groups are coordinated with other DERs in a distributed manner; on the bottom, TCLs in each group are controlled to provide the desired output collectively. The proposed method is a combination of economic and control techniques, in the sense that it synthetically captures the underlying economics from demand response as well as detailed dynamics in device level control.

For FY 2016, our first task is to design a distributed control algorithm based on push-sum + gradient technique to handle time-varying communication network topology. The proposed algorithm will be tested in switching communication networks. It is expected that the algorithm can handle communication time delays and packet drops, and we will run tests to examine the effectiveness and performance in this regard. Our second task will be evaluating and comparing distributed coordination algorithms using testbeds, in which we will select existing and proposed control algorithms for evaluation, implement control protocols in an agent-based fashion in co-simulation platform, specify communication network parameters and set up network simulators, and consider the experiment results as feedback for control parameter design or control algorithm improvement, as necessary.

Implementation of Extremely Large Scale Building Energy Simulation Infrastructure

Bing Liu

Although designed specifically for building energy efficiency problems, the infrastructure created in this project can be applied to virtually any simulation problem that involves a large number of complex workflows.

Existing tools for distributed computing and associated workflow management are inadequate to accommodate large-scale (millions of runs) problems efficiently. Generally, workflow management tools are either too simplistic, merely offering ways to push a large "N" through the system or are too focused on solving a specific issue, requiring programmer support to implement new or modify existing workflows. High performance computing (HPC) tools are generally designed and optimized for managing small numbers of large jobs rather than large numbers of small ones. The objective of our work is to accommodate a kind of computing problem that has been largely neglected in the typical user-facing infrastructures of HPC clusters: distributed problems involving large numbers of small jobs emanating from complex, potentially interconnected workflows.

This project addresses some of the above shortcomings, allowing a mix of independent and serially dependent jobs to be run efficiently and effectively on HPC systems without inordinately tying up computing resources or adversely affecting other (usually large) running jobs. It also provides straightforward tools for describing workflows and converting those descriptions into properly sequenced jobs on an HPC cluster. We anticipate that our work will enhance PNNL's ability to apply the ever increasing computing power available in HPC clusters and similar large-scale computing platforms to problems requiring simulation of massive numbers of cases.

This project met its objectives: an infrastructure design specified during the initial work was refined and improved; a software tool (named *Flood*) for managing large numbers of small jobs using a potentially dynamic number of compute nodes/cores was developed; a Workflow Description Language (WDL) for describing and defining the computing tasks necessary to address users' specific parametric analysis problems was designed; and a WDL interpreter was developed to convert users' workflow descriptions into manageable tasks on an HPC cluster.

The initial design was improved by eliminating the need for an external database management system for tracking the (potentially) millions of individual jobs in favor of a completely self-contained system. The necessity of multiple user-level tools and commands for managing partial runs, recovering from failed runs, and/or invalidating bad results was eliminated by exploiting modern disk monitoring tools.

The *Flood* software was implemented using the Python language, allowing the use of several existing modules/libraries to integrate all necessary functions into a single executable script. The WDL was designed to mimic the primary capabilities of the *make* software (of software development fame) closely, which many users at PNNL have used for three decades for similar work, while eliminating *make's* somewhat opaque syntax, difficult semantics, and inefficient implementation. Comprehensive documentation of the *Flood* software and the WDL were developed as part of this project.

The ultimate outcome of this work is a relatively simple software system compatible with PNNL's HPC clusters (but potentially extensible to other large-scale computing platforms such as cloud-based systems from Amazon) that accomplishes the following:

- allows users to define workflows using a language designed for the purpose
- acquires necessary computing resources through the normal HPC job management infrastructure but with the possibility of adjusting the number of nodes/cores during execution in response to cluster availability
- executes jobs, ensuring that serially dependent tasks run in the right order, with no performance/efficiency penalty for mixing long- and short-running processes
- tracks progress against the workflow definition so as to allow partial workflow runs (e.g., during development or for testing), intelligent restarts of failed workflow runs to avoid unnecessary rerunning of successful portions, and post-completion extension of workflow definitions without triggering reruns of already completed tasks
- accommodates dynamic acquisition and release of computing resources in response to cluster availability.

All goals envisioned for this work were achieved. We expect that as users exploit the system, some evolution of the software and infrastructure will be required. We anticipate that the system, perhaps with minor revisions, could be useful to those outside the building energy simulation domain in the future.

PN15034/2709

Integration and Demonstration of Co-simulation Platform in the CCSI Test Bed

Tess L. Williams

Our project has integrated a co-simulation platform into the Control of Complex Systems Initiative (CCSI) test bed, providing access to a flexible array of simulators that address domains such as power systems, markets, and communications.

The CCSI has begun to develop and implement an enduring test bed capability that provides an environment for testing at significant scale under a broad range of conditions to demonstrate and validate distributed control solutions for complex systems. Through this project, we have integrated and demonstrated a robust co-simulation platform in the test bed being developed by the CCSI. The goal is to establish PNNL as a leader in research in the field of distributed controls applied to large-scale complex systems, with a core element of this effort being the development of a powerful, flexible test bed. The CCSI test bed enables researchers who have developed new control schemes to examine whether the control achieves intended outcomes and if interactions directly or indirectly caused by the control system lead to unexpected consequences. This effort requires an experimental environment that can capture the macroscopic behavior of increasingly complex interacting systems with an adequate degree of fidelity.

Our project was responsible for integrating into test bed a co-simulation platform that coordinates simulations of power systems, communications networks, buildings and their systems, and markets. Central to the test bed is the Experiment Management System (XMS), which defines the workflow of experiments on the test bed, launches experiments, and will provide supervisory monitoring and database management. Additionally, we worked with the XMS-development project to define requisite and standard interfaces for integrating simulators into the XMS; e.g., the requirement that simulators must allow an external actor to access and control the timestep of the simulation order to establish synchronization between simulations.

We worked closely with a project focused on improving and adding capabilities to an existing co-simulation tool (PNNL's Framework for Network Co-simulation [FNCS], which has been developed through investment of the Future Power Grid Initiative). FNCS is a prototype implementation of a federated co-simulation environment targeted to power grid and communication network simulators. In order to boost performance, it made limiting assumptions about the simulators involved, which inhibits its usefulness in the currently proposed project. However, portions of the software were reused with respect to the application interfaces and the central "broker" application. Together with that effort, this project determined the simulation requirements for supporting the use cases of current and anticipated future experiments. As part of this work, an abstracted interface was designed to allow the co-simulation platform greater flexibility and scalability in communicating with initial target simulators as well as a more simple process for interfacing with additional simulators as they are tied into the test bed and made available for experiments.

As noted previously, this project worked with the XMS-development project to begin to develop the technical requirements for a data management process for the co-simulation platform. The project work included identifying data streams that need to be updated to the XMS as an experiment progresses and the data required to be stored locally to each simulator and made available to the XMS for analysis after an experiment concludes, based on bandwidth and performance limitations.

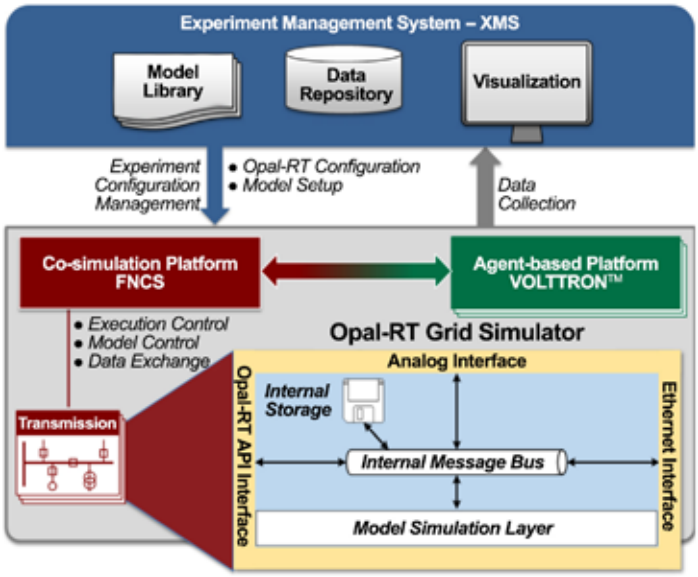
PN15006/2681

Integration and Demonstration of Scalable Power System Simulation for CCSI Test Bed

Mallikarjuna R. Vallem

This project will enable researchers to assess the behavior of bulk power system to several control components in simulation and real-time experimentation by integrating a robust power system simulator into the Control of Complex Systems Initiative (CCSI) test bed.

The CCSI test bed envisages integrated experimentation platform for distributed buildings and buildings to electrical system control components. A robust commercial real-time digital simulator that perform grid simulation, Opal-RT is integrated into the CCSI test bed to provide bulk-grid behavior to several controls components. This integration provides experiment control and synchronization of Opal-RT with experimental management system (XMS) as well as data exchange with the Framework for Network Co-Simulator (FNCS). Most bulk-grid models are available in industry standard formats such as PTI RAW. There is significant burden associated with model preparation for Opal-RT simulations from the standard formats. To this end, our project developed model conversion and validation templates to reduce experimenter burden in order to use the Opal-RT grid simulation.



Opal-RT integration for bulk-grid simulation

The focus of the project during FY 2015 has been on integrating the Opal-RT into the CCSI testbed to enable non-real-time bulk-grid simulation capabilities. This work primarily involved the following tasks.

Adapting the Opal-RT application program interface (API) to control simulation on Opal-RT simulator. The Opal-RT system includes a target on which the simulations are performed and a host that is used to prepare the experiment and both control and visualize experiment. The simulation in the target machine is controlled from the host using a customized python API developed by Opal-RT Technologies. It is first of its kind to integrate the Opal-RT simulation with other simulators directly and synchronizing not in real time. The functions available in the API are then adapted into python libraries to enable control of the simulation in the co-simulation environment.

Creating a Linux-based Opal-RT host. Typically, Opal-RT simulations are controlled through an application called RT-Lab, which runs on a Windows host. Because the FNCS and XMS components were created for Linux- based virtual machines, it is desirable to create a Linux VM and Opal-RT host. The Opal-RT customized Linux VM was created with the support of Opal-RT Technologies. The developed python API libraries have been successfully tested with this Linux VM.

Interfacing Opal-RT simulation with FNCS. Python wrappers have been provided for FNCS co-simulation for use with the Opal-RT API. In turn, these wrapper functions have been integrated with the adapted Opal-RT API libraries to enable data exchange and synchronization with FNCS. This interface has been successfully tested.

Interfacing with XMS. XMS provides the experiment setup; therefore, the Linux VM has been developed to be compatible with XMS. This work included functions like instantiation, cloud access for setup with FNCS and other co-simulators, and termination of the experiment. Appropriate heat templates were also developed for instantiation by XMS. In addition, python libraries were developed to translate XMS functions to Opal-RT VM.

During FY 2016, we will perform integration and testing with XMS and FNCS for real-time experiments. This development will complement the capabilities of FNCS to perform real-time experiments and synchronization. Moving from stand-alone testing of Opal-RT integration with XMS and FNCS, we will test multiple co-simulators with Opal-RT to analyze and improve the integration of grid simulation for the CCSI testbed. Finally, use cases will be developed for demonstration of the CCSI testbed with multiple co-simulators.

PN15005/2680

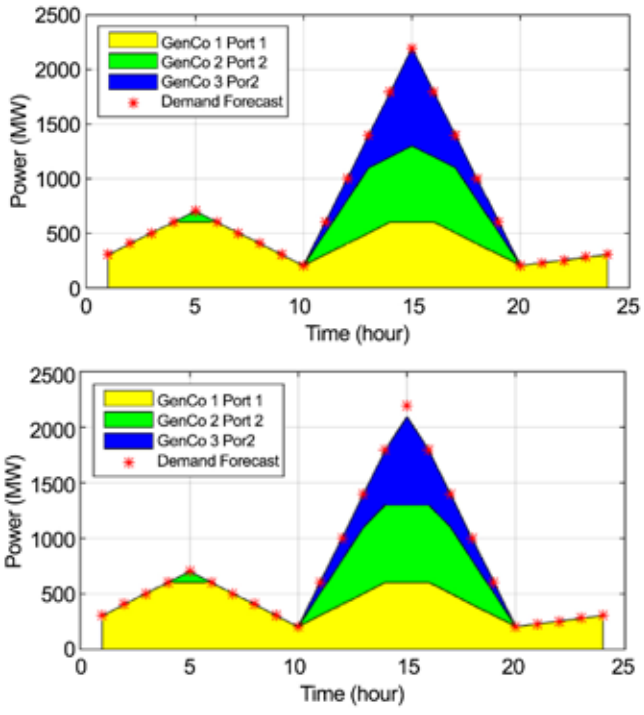
Market Design Analysis Tool

Abhishek Somani

We are investigating various mechanisms that need to be established at the retail level to help coordinate and control responses.

Starting at the bulk power system level, the value of operational flexibility is increasing due to elevated penetration of renewables and distributed energy resources (DERs). Proliferation of DERs also present challenges to distribution system operators and utilities, as it may not always to be possible to control every device directly. Hence, it is important to study retail market mechanisms and the interaction with wholesale markets.

This project is designed to take an end-to-end view of the power system. Distribution level assets (including demand-response), distributed generation, and energy storage can be used to provide grid services (energy and ancillary) to manage intermittency due to renewable sources. The incentives for demand side resources to provide the needed flexibility may be derived from provision of grid services, which requires appropriate modeling and monetization of these services and rules for participation of distribution level assets in the wholesale markets. However, the use of demand-side resources will not proliferate lest they are controllable to avoid additional uncertainties.



Dispatch for market participants without (top) and with (bottom) participation by flexible demand-side resources.

AEP gridSMART demonstration used a double-auction based transactive control mechanism to coordinate responses of residential HVAC systems. However, given the relatively low number of participating households, the impact of these responsive assets was minimal in both the physical system and in the wholesale markets. It has been shown that participation by a large enough number of responsive demand side assets can have an impact on wholesale markets, creating instability in the system. Hence, modeling bidding behavior of a load serving entity (LSE)/aggregator to represent aggregated demand side assets in the wholesale markets is another challenging issue that this project addresses.

The wholesale power markets have undergone substantial change over the past few years to deal with increasing penetrations of variable energy resources. The market design and processes have become more complex from the introduction of new products and services to deal with the variability and intermittency of renewable resources. Additionally, the increasing adoption of DERs presents new challenges for the power grid operations that requires some additional flexibility in order to ensure the most stable, reliable, and resilient grid operations. The current market designs, however, do not adequately treat flexibility from resources. For our work in FY 2015, we formulated a novel unit commitment/economic dispatch problem formulation that explicitly values the flexibility offered by resources. The market design is based on the concept of two-part pricing, where resources are first paid to make their capacities available (including the flexibility) in the day-ahead markets as well as a subsequent performance payment based on real-time dispatch. The mechanism involves the use of standardized contracts, which allows the procurement of energy and reserve capacity using a single market clearing auction instead of a separate auction for every commodity.

Having a standardized contract (SC) for energy and reserves obviates the need for market participants to submit separate bids for various commodities along with clearing a single market for capacity, as opposed to a separate market for each commodity. We also extend the SC design for demand side resources. These resources, which may be a combination of demand response, distributed storage, rooftop solar, and the like, can offer their flexibility to aid in system operations. Specifically, the LSE/aggregator can participate in the wholesale market by offering a flexible net-load curve in the day-ahead energy markets.

PN13029/2510

Multidimensional Membrane Theory to Predict Power System Oscillations

Laurie E. Miller

This work will link power system electrical configuration to oscillations so that the latter can be predicted and avoided at the grid planning and operations stages for greater robustness and resilience.

Our research applies the concepts of multi-dimensional oscillating membranes, similar to that used in the "theory of everything" (M-theory) in modern physics, to formulate a new model of electric power grid dynamics and oscillations, forming a topology-based dynamic characterization. This new model could lead to a completely new physical understanding and new models of the system, leading the way to a new generation of grid analytics and applications, particularly improving grid resilience in the face of increasing complexity, uncertainty, and variability from major outages, storms, and other events. This project addresses a completely new idea of using multidimensional oscillating membranes to explain and describe power system dynamics, including inter-area oscillations. It will produce new insights to explain and visualize the nature and reasons for these oscillations.

Low-frequency oscillations can and do occur during interchange of power between neighboring regions or areas of operation. These inter-area oscillations remain a challenge for grid analysts, despite being a problem of long standing. With increasing power system size and complexity, designing for a robust and resilient system becomes a larger and more complex problem as well. Inter-area oscillations add a difficult extra layer of complexity in power system planning because they are a phenomenon that can be spontaneous, is not well-understood, and lacks predictive, actionable mitigation.

The core idea behind our proposed oscillating membrane theory of a power grid is that in an electrical and electromechanical sense the grid has a different topology compared to its 2D layout on the earth's surface. A realistic power grid would not necessarily have exactly two or exactly four nearest neighbors; effort is being expended to explore how the mathematics changes for systems of three and six nearest neighbors. By allowing geographically distant points to be brought close by high-voltage transmission lines (just as an interaction in M-theory is a topology-changing event), the resulting image of the grid in the electrical sense can be represented as a multidimensional membrane, which oscillates over time. Our hypothesis is that this membrane has certain natural frequencies while oscillating in a multidimensional space. The actually observed free oscillations are excited by small or large perturbations of system parameters and can appear or disappear with changes in system configuration. Oscillations can also be forced by periodic forces stressing the membrane.

The key technical challenge for the first half year was to establish a link between system size and oscillatory modes for systems of a linear topology for systems of a rectilinear mesh topology. In addition, we wished to establish an analogous link between system size and oscillatory modes for systems of a loop and cylindrical topologies and to study the changes in oscillatory modes, as these topologies change in size and are linked from lines into rings or from rectangles into cylinders.

This effort was successful, and an analytical expression for this relationship was found for the cases described. The situation allows for the prediction of oscillatory behavior as a function of system topology in a manner that was not previously available. The evidence is that for many types of warping the 2D rectilinear system into three and four dimensions a closed-form expression does exist, but finding those expressions will have to be tabled for future research so as not to delay the aims of this project. An extended abstract for publication related to this work has been accepted, and the full paper is in preparation.

New lines of inquiry have been and are being identified in this investigation. We encountered evidence of singularities in the voltage stability region of power systems under stress conditions, a phenomenon not yet known in the published literature. We confirmed that such singularities exist in a realistic system in another project but ran across them by accident and luck. A next step is to theorize how the methods used in this project could make the leap from inducing such singularities to predicting them. There may not be time to explore this adequately, but it may form an important new line of inquiry in its own right. Thus, our efforts in FY 2016 will focus on expanding on these lines of inquiry and demonstrating the patterns in how system oscillations change in much larger test systems as the system topologies change under new operating conditions.

PN15046/2721

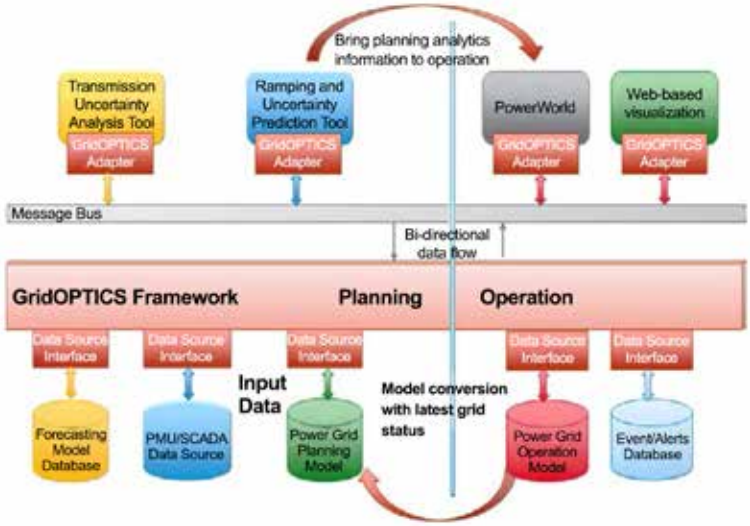
Operations and Planning Fusion

Yousu Chen

This project advances decision support for the next generation of power system operation by integrating analysis results from planning into real-time operation and improving planning functions with fresher, more accurate operation information.

The U.S. power system is accommodating new intermittent power generation technologies, controlling paradigms, and supporting the deployment of automation technology at all levels of the system. With this dynamic behavior brings the burdens of incorporating the predictive capability from planning to enhance today's power grid operation. These pressures are manifesting themselves in a more smooth integration between the functional roles of planning and operations.

The goal of this project is to provide an initial set of tools that enable a bi-directional exchange of data between operations and planning environments based on existing integration and messaging framework developed under the GridOPTICS™ software system (GOSS). These tools should allow the results of traditionally operational planning studies to be reflected in relevant real-time tools available to the system operator and support initialization of the planning analysis tools with current data from the operational system. By understanding scenarios that drive the interplay between operations and planning, we will articulate a set of common tools to help bridge these two worlds. While the objective can service a large number of operational scenarios, the project is structured to identify a core set of capabilities that can demonstrate the bidirectional flow of information in a small subset of scenarios. The outcome will reduce the difficulty with integrating operations and planning while respecting the natural differences between their domains and design centers.



Software component design of operation and planning fusion built on the GridOPTICS™ framework.

In FY 2013, we successfully evaluated a set of candidate tools and selected an uncertainty analysis (ramping) and transmission tool to support a set of illustrative use cases that demonstrate the benefits of operation and planning fusion. For FY 2014, we continued our effort of system design and requirements identification for extensions to the GridOPTICS™ framework needed to support the information exchange between planning and operation for the identified use cases. Two demonstration cases based on the ramping tool were developed to show the usability of the overall project framework and to establish that the fusion of planning and operation can help provide better decision support and improve system reliability. These demonstration cases involve four tools that have been integrated on the GOSS framework and can communicate to each other: 1) a ramping engine tool to read forecast data from GOSS, create predictive ramping capacity data, and archive the data to the GOSS database; 2) a web-based visualization tool to visualize the ramping outputs from the GOSS database; 3) the PowerWorld tool to present system status from the operation side; and 4) a conversion tool to transform the node-break to bus-branch model.

In FY 2015, we successfully integrated the ramping tool with PowerSimulator based on the GOSS framework, along with the web-browser-based visualization tool. A user study experiment was conducted to evaluate the effectiveness and usability of this tool through operator training classes by the North American Electric Reliability Corporation certified operators, who reported that the tool could provide valuable information to help them determine the deficiency in generation capability quickly and aid in their decision-making process, especially under emergency conditions. This user study validated the usability and effectiveness of the developed tool.

Besides the ramping tool, the transmission tool was successfully integrated with the GOSS to predict possible congestion and voltage reduction problems caused by the uncertainty of renewal energy and loads. A paper based on this work was accepted by the International Federation of Automatic Control and will be presented at its annual symposium that will take place during FY 2016.

PN13091/2572

Resilience in Large-Scale Distributed Control Systems

Wei Zhang

This project aims to develop a unified approach systematically to quantify, analyze, and improve resilience of a distributed control system. The research is expected to yield new design principles and tools for the future power system with a more distributed control architecture.

In many parts of the future power systems, distributed control arises naturally. Using distributed control will create tremendous opportunities to improve system performance but at the same time introduce stronger couplings among systems. For such a system, local faults or attacks are more likely to propagate and impact the rest of the network, making it challenging to ensure the resilient operation of the overall system. This project aims to formally quantify and analyze resilience for distributed control systems with an emphasis on applications in resilient power system operations and resilient control of distributed energy resources (DERs) in microgrid. We are particularly interested in understanding whether a distributed control system can still perform well after abrupt changes to the system structure. This concept is fundamentally different from the traditional ideas about stability and robustness, which mainly focus on system dynamic behaviors under continuous disturbances.

During FY 2015, we first reviewed the literature on resilience of distributed control systems. For power system applications, there is a vast amount of resources that have covered stealthy attacks and their impact on state-estimation data integrity. The results have also been recently extended in the control community by incorporating system dynamics, which allows for fast detection of attacks, bad data, or even line failures using phasor measurement unit data. Although these studies provide more sophisticated tools for secure monitoring of distributed systems, they do not quantify the overall resilience property of the system. In addition, the dynamic extension studied in the control community are mainly based on the existing fault detection/identification methods with deterministic system models. More recently, some preliminary ideas have also been proposed for general control systems to quantify the overall closed-loop control system risk under different attack scenarios. Such results are often based on overly simplified models for system and control strategies.

Also in FY 2015, we developed a unified approach to enable systematic analysis of resilience for general distributed control systems. We proposed a graph-theoretic model to describe distributed control systems that graph captures the cyber and physical couplings among the different subsystems. We also proposed to view various distributed control design problems as distributed optimization problems, where the control objective is encoded in the cost function and design requirements (including stability requirements) that can be translated into the constraints of the optimization problem. Based on the system and control model, we proposed a unified way to quantify system resilience, for which the contingencies (attacks or failures) are modeled as perturbations to the system graph, and the resilience is quantified by the amount of deviation of the cost function after a contingency event. This approach can be applied to study various power system applications and has been tested using the IEEE 30-bus system in MATPOWER, for which we simulated the impact of all possible attacks/failures on the transmission lines with cardinality of 2 under different control strategies. Most of the attacks resulted in cascading failures, some of which lead to more than 40% of load shedding. We show that with proper re-dispatch of the power, the amount of load shedding can be significantly reduced. The corresponding resilience improvement has also been quantified and calculated.

In addition, we have begun to tackle the problem of attack/fault detection and identification, which is one of the most crucial components of a resilient distributed control system. Different from many existing studies, we study the problem by incorporating dynamics and probabilistic uncertainties and emphasize on those failures/attacks that change the system graph rather than simply altering some sensor data. We are currently working on extending the classical change point detection methods to solve this challenging problem. Such research is expected to lead to advanced monitoring algorithms that can incorporate system uncertainties and detect contingency events quickly to enable fast, effective remedial actions.

In FY 2016, we will fully develop the probabilistic approach for attack/failure detections for distributed control systems. We will test the method for realistic applications in power system and microgrid control systems. In addition, we will extend our current optimization-based resilience metric to incorporate the developed detection algorithms. We expect to be able to discuss the impact of different detection/control methods on the resilience of the overall distributed control system.

PN15007/2682

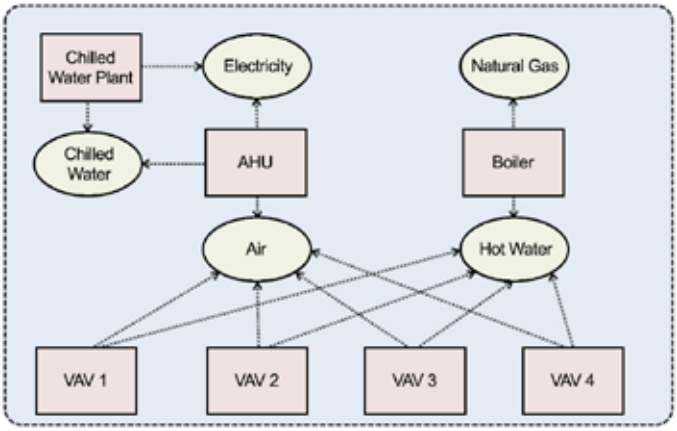
Transactive Control of Commercial Buildings for Demand Response

Charles D. Corbin

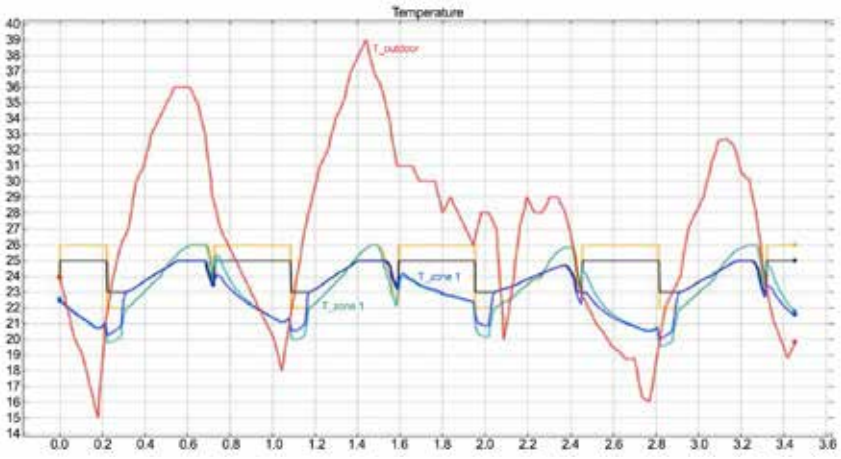
We developed a transactive control approach to achieve demand response in commercial building heating, ventilation, and air-conditioning (HVAC) systems.

A type of distributed control strategy, transactive control uses market mechanisms to engage self-interested responsive loads to achieve power balance of supply and demand in the electrical power grid. Transactive control aims at coordinating seamlessly the operation of large numbers of new distributed energy assets (DERs), such as distributed solar, energy storage, and demand response from residential and commercial loads to provide the flexibility for operating the power grid reliably and at minimum cost in the presence of large amounts of intermittent renewable generation. Compared to traditional direct load control (DLC) approaches, transactive control solutions emphasize a decentralized method in which consumer and third-party decision-making are kept local and private to manage large-scale deployments (with eventually hundreds of millions of individual assets) while maintaining consumer free will. This approach also addresses the key challenge of providing smooth, stable, and predictable "control" of these assets, despite the fact that most are neither owned nor controlled by the power grid.

We focused on applying transactive energy concepts to components within a commercial building as a model for enabling collections of buildings to trade and negotiate energy consumption through transactions. For example, at the building level, air-handling units (AHU) "purchase" hot and cold water from the boiler and chiller, and "sell" cooled supply air to the variable air volume (VAV) boxes connected to the conditioned zones, which adjust zone thermostats in order to adjust the bid quantity. In particular, this project applies the transactive energy concept to the individual components of the energy systems within the Systems Engineering Building (SEB) to realize reduced energy use and cost and allow for increased flexibility in managing electric demand. This approach is hypothesized to result in an optimal response to demand events because system constraints are communicated down through the meter to the individual actors in the system, allowing all actors within a building to participate collectively in addressing these constraints. Results from this project will inform the Clean Energy and Transactive Campus (CETC) project and provide the foundational models, market mechanism, and control algorithms necessary to investigate the potential for intra-building transactive control to provide demand response and regional electricity balancing services when applied to a collection of commercial buildings.



Transactive markets (green ovals) and agents (pink rectangles) within a typical commercial building.



Two zones compete for cooling by adjusting set points according to a dynamic incentive signal.

We first identified the agents and commodities that would be represented in the building transactive market, then defined three market structure variations that represent different levels of complexity. In the simplest variation, VAV boxes (building zones) bid for chilled air supplied by a combined AHU/Chiller agent,

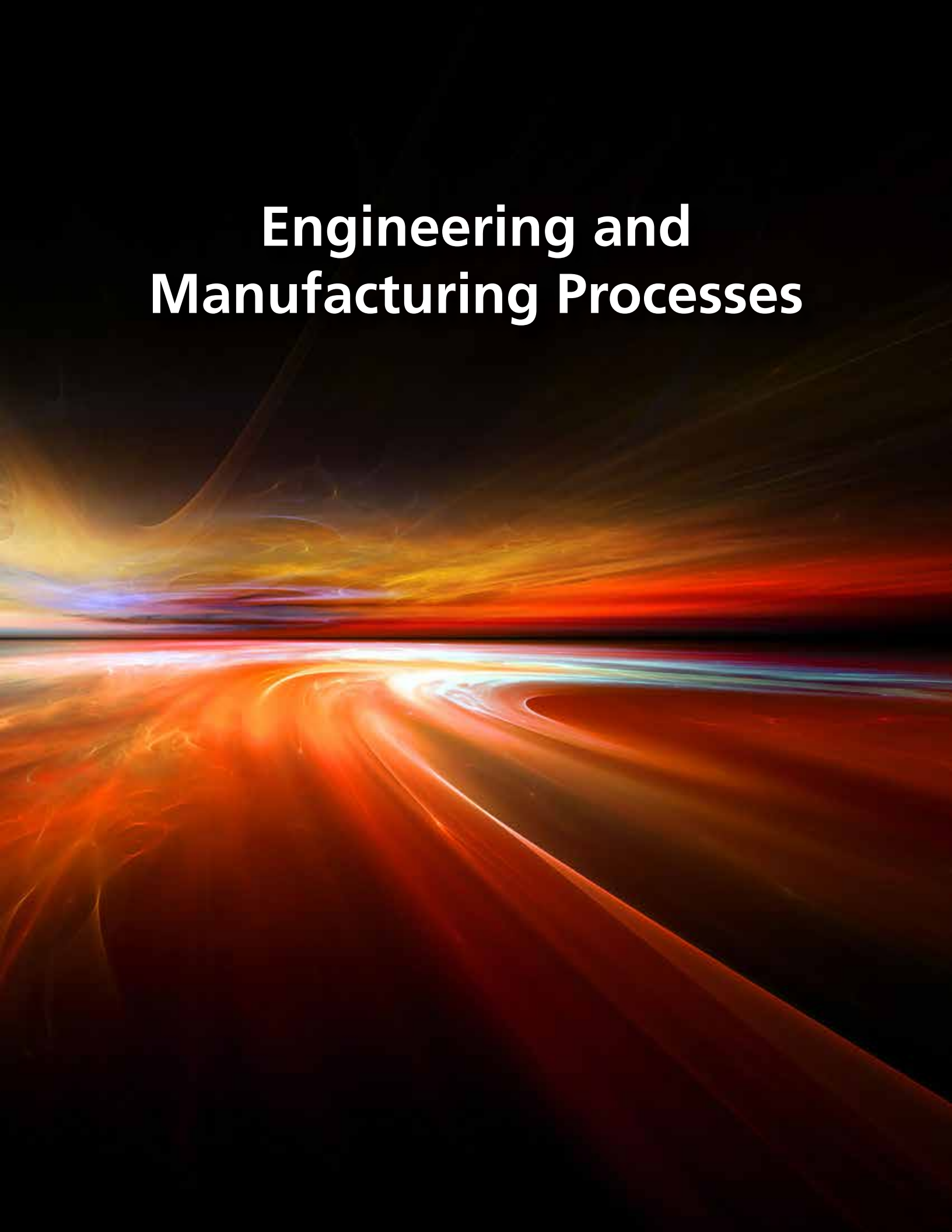
PN15075/2750

which then bid for electricity from the electric meter. In the most complex variation, the AHU/Chiller agent was disaggregated into separate agents, and a boiler plus three markets for chilled water, hot water, and natural gas were added. Reduced order models for each of the HVAC components, including AHU, chiller, boiler, and building zones, were defined. A detailed EnergyPlus model of the SEB was constructed using information from construction drawings and discussions with facility staff. The model was necessary for testing transactive market structures prior to algorithms being deployed to the building automation system (BAS) and for assessing the demand flexibility of the building under different conditions. Monitored data from the SEB was collected from the BAS to calibrate the detailed EnergyPlus model and reduced order models used by the market agents. Markets and agents were coded in Python and integrated with the detailed SEB model using a co-simulation environment. Finally, a mock-up of a building dashboard was created to give building managers insight into control actions and energy impacts.

The combined market and SEB model was subjected to several experiments to study the behavior of the transactive control system over a typical summer week. These experiments included the following cases: 1) the SEB was given a not-to-exceed demand limit; 2) the building was provided a historical real-time price signal; 3) the building was given a dynamic signal representing electric system load imbalance; 4) the building market operated independently of external price or demand limit. The market mechanism resulted in reduced peak HVAC electric demand measuring 9%, 8%, 5%, and 6%, respectively, for the four cases. Energy savings results were mixed with an increase of 1% in case 1, a decrease of 8% in case 2, and no change in cases 3 and 4. Inspection of case 3's demand time series revealed a limited but not insignificant ability of the market adjust building demand in order to track the imbalance signal.

Contributions of this work include 1) a new transactive market scheme that results in predictable cleared quantities without price/quantity iteration; 2) a general method for clearing multiple, dependent markets without requiring explicit knowledge of the market structure; 3) a Python prototype that can be easily implemented in VOLTTRON™ and deployed to control the SEB; 4) an assessment of the SEB's electric demand flexibility; and 5) a foundation for future study of transactive building control in the CETC project.

Engineering and Manufacturing Processes

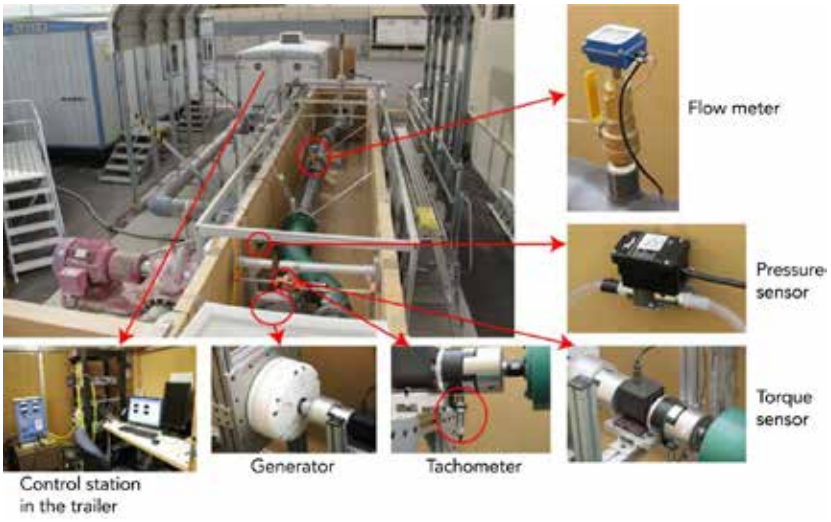


Composite Turbines for Small Hydro

Zhiqun Daniel Deng

We are developing a cost-effective manufacturing method to demonstrate the feasibility of small hydro turbines made from fiber-reinforced composites.

Although composite materials have seen use in hydropower systems, they are primarily employed to date in some pilot-scale tidal turbines and hydrokinetic river systems. There remains a lack of knowledge about using composite turbines in small hydropower systems and how the mechanical properties of composite materials are related to the performance and durability of these turbines. We are developing a cost-effective manufacturing method and forming the knowledge base about how the mechanical properties of these materials are related to the efficiency and durability of the turbines. After feasibility is demonstrated, other funding sources or a follow-on project will be pursued to develop a comprehensive evaluation (such as non-destructive health monitoring) and modeling tools (such as a cavitation prediction model). The successful development of these composite turbines will significantly facilitate the adoption and deployment of small hydro systems in many remote areas where hydro power has been unable to reach.



The closed-loop turbine performance model

Small hydropower systems convert mechanical and potential energy from flowing water in small rivers or irrigation canals with low heads (height of fall of water) into electricity without the need of costly facilities and can be readily constructed in remote or rugged locations where a full-scale hydroelectric dam system is not feasible. With conventional stainless steel as the turbine material, constructing small hydropower systems at those locations remains hindered by the heavy weight and difficulty to transport and maintain. Composite materials can overcome these challenges and greatly improve the feasibility of deployment from their significantly lighter weight compared with steel. Moreover, the lighter weight of composite turbines allows them to spin and generate electricity at lower water flow speeds compared to steel turbines.

The objective of this effort was developing a cost-effective manufacturing method to demonstrate the feasibility of small hydro turbines using composites, establishing a scale turbine test facility, and evaluating the performance of the prototype scale turbine. The project was performed in two stages: the selection of composite material and fabrication of the scale turbine; and testing of the prototype scale turbine using a scaled-down hydroelectric setup.

We developed a lightweight polymer composite turbine blade for low head hydroelectric applications. Structural modifications to a common steel Kaplan style blade was designed using computational drafting software to provide increased strength to high stress regions on the blade. Using a simple linear elastic isotropic model, an optimized design with a minimized tip deflection and lowered stress concentrations was developed. Modeling verified the design and met efficiency targets, and further ANSYS® structural modeling created a refined model for the root section to compensate for the lower stiffness of the composite material. The final design resulted in a 35% increase in volume while reducing mass by 81%, matching the predicted blade efficiency.

We set up a scale turbine facility outside PNNL Aquatic Research laboratory, a closed-loop hydroelectric turbine performance model. The flow loop includes flow rate and pressure measurement devices for turbine efficiency testing. A torque meter and tachometer are attached to the output shaft of the turbine for output measurements. The instrumentation and test procedures were performed according to the International Standard defined by IEC-60193, the standard for the model acceptance tests for hydraulic turbines, storage pumps, and pump-turbines. The prototype turbines were successfully evaluated for the main hydraulic performance variables.

Ultimately, we successfully demonstrated the feasibility and our capabilities of developing a cost-effective composite turbine for small hydro. We also established the capability of conducting performance evaluation of scale turbines.

PN15042/2717

Graphene Oxide Based Structured Laminar Membranes

David W. Gotthold

By developing a fundamental understanding of how new laminar membranes function and assemble, we will enable the development of practical water separation membranes.

Structured laminar membranes consisting of hierarchically stacked overlapping layers of 2D graphene oxide are a fascinating and promising new class of materials with potential for radically improved water separation with excellent selectivity and high permeability. Our project was based on published results that showed that graphene oxide (GO) has significant potential as a highly selective membrane for water vapor, with selectivities above 10^{10}. To enable practical applications for this new class of structured materials, two key fundamental issues must be resolved. First, the mechanism responsible for water transport in laminar membranes (such as GO) needs to be identified as well as the influences of structure and surface chemistry on the transport properties. Second, the laminar structure assembly needs to be determined to develop a scalable synthesis route to make commercially viable separation membranes.

In FY 2014, we focused on evaluating the basic material properties such as graphene flake size, membrane structure, and permeability. We determined that larger flakes produced more physically robust membranes with higher selectivity and permeability. We had two focus areas in FY 2015: first, we used the knowledge on flake size and process chemistry previously developed to enable a scalable synthesis process. Second, we continued to develop a better understanding of the surface chemistry and structure through advanced characterization and modeling.

Our team focused on the simple preparation of scalable GO membranes with large GO flakes by a gel method because the modified Hummer's method produces small sizes of GO flakes due to vigorous stirring during the oxidation process, and it takes long time to wash metal ions and acid during the dialysis. Further, this approach has a limit to make large-scale GO membranes. The gel method is quick and easy, and large GO flakes are maintained even after the process, which is a key for scalable GO membrane formation. Large, uniform 500 µm graphite powder was used as a GO precursor, and ~200 µm size GO flakes were observed in GO dispersion after the process.

GO gel dispersion (3–5% in water) is stable (homogeneous) and easily casted on a Teflon plate. GO gel dispersion is carefully poured onto the plate and spread with a glass rod. Thickness and size of GO cast membranes are easily controllable. Free-standing GO membranes are peeled off using a tape when dried; thin, large GO membranes are possible (2 µm thick and >20 cm long). One large GO membrane was used for characterization (XRD, FT-IR, SEM, XPS, TGA, and stability in different solvent mixtures) and a performance test (water vapor permeability from gas mixtures). Additionally, these membranes were evaluated using mixed gas permeability testing (with O_2, N_2, CO_2, and H_2O) and exhibited very high selectivity for H_2O with N_2, O_2, and CO_2 at or below the system measurement limit, correlating to a selectivity ratio for water greater than 10^4. The H_2O vapor permeation rates varied across two orders of magnitude,

A large (~500 cm^2) graphene oxide membrane formed using a scaleable casting process compared to a standard vacuum filtration membrane.

PN14050/2634

depending on GO precursors and preparation methods, with a peak around 1.01×10^{-5} mol/m^{2}sPa (2.3×10^5 Barrer). In addition, we have begun modeling the vapor transport properties and correlating with the observed variations.

A sequence of quantum and classical simulations were performed to probe the behavior of the water confined between the layers as well as the interaction of the water with the functional groups in the membranes. Classical molecular dynamics simulations of model graphene oxide systems were performed, containing intercalated water molecules to understand the mechanisms driving rapid water transport. The simulations considered six different hydration levels. The simulation cell had 45000 to 65000 atoms with a C/O ratio of 4 and hydroxyl group functionalization. The layer spacing was found to vary from 8 Å in dry membrane to 11 Å in well-hydrated membrane, in good agreement with experimental observations. With increasing hydration, the proportion of free water molecules increases, with these molecules moving away from hydroxyl groups. *Ab initio* modeling of a by-layer of the membranes with C/O ratio of 4 and hydroxyl or epoxy group functionalization embedded into a water solvent in a periodic system show that at room temperature, Grotthus proton transfer events can occur between the water molecules as well as proton transfer from the water to the GO_x layer and between functional groups on the flake.

For FY 2016, work will continue to extend the understanding of the interaction between surface chemistry, structure, and performance by using advanced characterization and modeling. We will explore practical applications by building and demonstrating dehumidification and dewatering filtration systems.

Interfacial Engineering: A Theory Based Approach to Join Dissimilar Materials

Vineet V. Joshi

We are developing novel tools to predict the interface needed to join dissimilar alloys via solid or molten state that will limit the galvanic corrosion rate while retaining the joint properties.

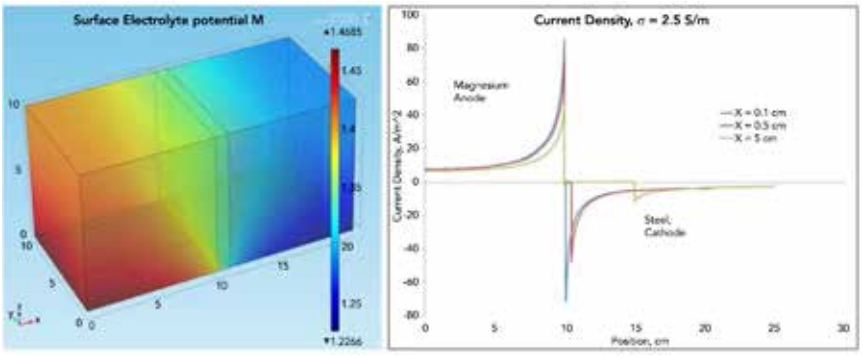
No system in its entirety can be developed out of single material. Design engineers are increasingly faced with the need to join dissimilar materials as they are seeking creative new structures or parts with tailor-engineered properties. Widely different physical characteristics (melting point mismatch, coefficient of thermal expansion, etc.) and chemical incompatibility (presence of galvanic couple, chemical reaction at the interface) make dissimilar material joining a challenging task. The applications of these materials systems are needed in all the emerging fields such as power electronics, fuel cells, automobiles and aerospace. As an example, magnesium alloys owing to their high specific strength is widely being investigated for a range of structural applications such as in automotive, aerospace and electronics packaging. However, the application of magnesium alloys gets limited in multi-material systems because of the poor corrosion resistance. The most anodic of the structural materials, magnesium is susceptible to galvanic corrosion and disintegrates severely when interfaced with popular structural alloys such as aluminum and steel.

Conventional techniques of joining such as mechanical fastening, adhesive bonding, welding, and the like are being developed to overcome this problem. However, a sacrifice in either strength or corrosion rate is usually accompanied with it. Additionally, coatings of zinc, cadmium and Teflon/other polymers are also used on magnesium alloys at the interface of the two mating surfaces, which also comes at a cost penalty. Apart from being susceptible to galvanic corrosion magnesium alloys are also the least wear resistance. The aforementioned coatings being applied on magnesium alloys are also accompanied by maintaining a clean zone free of abrasives, fluxes, and oils that are commonly used to clean, weld, and lubricate during component manufacturing because magnesium is susceptible to other forms of corrosion and wear in their presence.

We are developing alloys that readily bond with the magnesium alloys and the other faying surface. The salient feature of this work is the creation of a graded galvanic interface that will improve the corrosion resistance and maintain joint strength. The newly developed alloy can be used further as coating and can be extended into the exposed magnesium component to prevent other forms of corrosion and abrasion. Both fusion-based (brazing) and solid state joining (friction stir welding) techniques would be implemented to investigate the effectiveness of this interlayer. The process would combat the galvanic corrosion issue and concurrently develop a bond that has good mechanical properties, thus eliminating the cost of multiple processes being used presently to join the two systems.

From our work in FY 2015, we demonstrated that creating a galvanically graded surface helps in reducing the corrosion rate by an over an order of magnitude. COMSOL multi-physics was used to predict the corrosion rate as shown in the accompanying image. The developed tool will be important not only to join the two materials but also used for coatings. Complex geometries and shapes common with engineering applications can also be evaluated using this tool. It was determined that along with strength (stress-strain curves), if we can obtain the Tafel plots, we can design the structures systematically. Using the shear-assisted indirect extrusion, such an interface can be created.

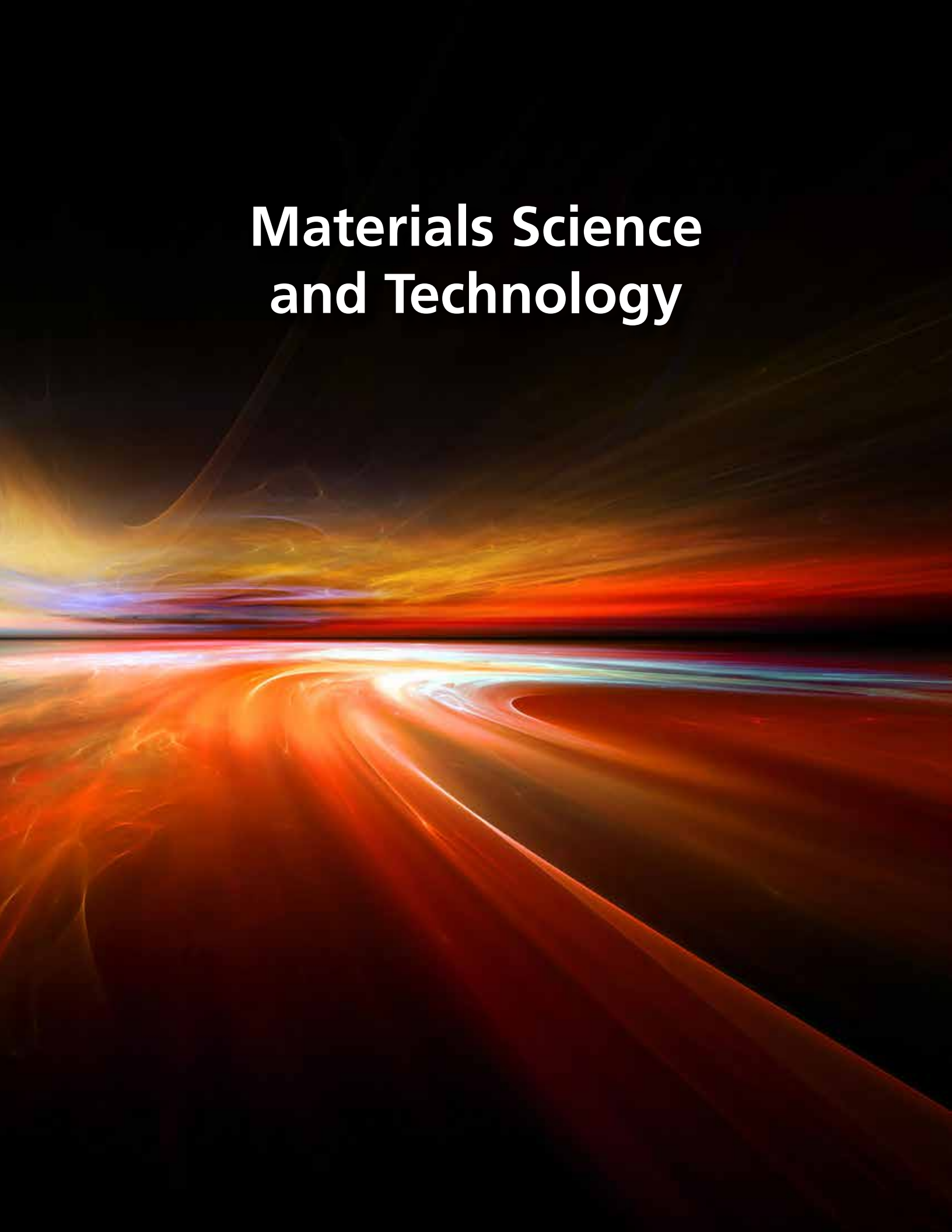
Throughout the year, we successfully demonstrated a computational approach to predict and prevent galvanic corrosion in metallic joints. In addition, galvanic corrosion of magnesium by steel can be improved by an order of magnitude by introducing a galvanically graded interface, and a method to form such galvanically graded interfaces was demonstrated.



The schematic of a computational domain and potential across the electrolyte and the initial spatial current density variation predicted using the numerical model to estimate the corrosion rate.

PN15062/2737

Materials Science and Technology

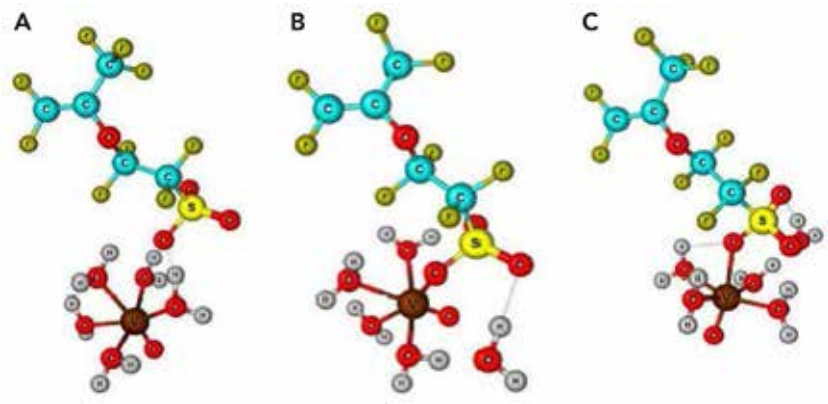


Atomistic View of Solid-Liquid Interfaces Using *In situ* X-ray Probes

Vijayakumar Murugesan

Our work is developing a unique imaging capability based on X-ray microscopy that can provide unprecedented chemical imaging of interfaces.

Molecular interactions at the heterogeneous interfaces such as solid-liquid interface are pivotal to energy storage processes; however, predictive understanding about the impact of solvation phenomena, electrode surface chemistry, and kinetic process on their interfacial interactions is seriously limited. More specifically, a lack of comprehensive understanding about interactions between Nafion membrane and battery electrolytes prevents the straightforward tailoring of optimal materials for redox flow battery applications. In this work, we analyzed the interaction between aqua-vanadyl cation and sulfonic sites within the pores of Nafion membranes using combined theoretical and experimental X-ray spectroscopic methods.



Schematic view three possible interaction mechanisms, namely (A) solvent share, (B) contact pair through cis position, and (C) contact pair through trans position between solvated vanadyl ion with sulfonic acid sites inside the Nafion pores based on density functional theory (DFT) analysis.

The vanadyl ion normally exists as a distorted octahedral structured cation $[VO{\cdot}5(H_2O)]^{2+}$ in aqueous solution. This cation has five liable water molecules in octahedral coordination, along with one vanadyl oxygen (V=O) that constitutes the first coordination sphere. The aqua-vanadyl ion can diffuse into Nafion membranes, forming electrostatic interactions with negatively charged sulfonic acid sites within the membrane pore structure. The diffusing aqua-cation can interact through the solvent share mechanism where the water molecule from first solvation can interact with sulfonic site through hydrogen bonding interaction. Alternatively, the sulfonic site can directly bond with the central vanadium atom via V-O bonding. This direct bonding represents a contact pair mechanism where the symmetry of the bond with respect to the native V=O can result in either *cis* or *trans* positions. Schematic view of optimized geometry for solvent share, *cis*, and *trans* contact pair mechanisms are shown. To evaluate these three different possible vanadyl ion specific interactions and possibly identify the dominant mechanism within Nafion pores, we took XANES measurements on pristine Nafion, vanadyl ion solution, and soaked Nafion membrane.

The vanadium K-edge spectra of pure vanadyl ion electrolyte solution and soaked Nafion membrane show very similar spectrum with pre-edge absorption peaks (A and B) followed by shoulder peak (C) on strong absorption curve (peak D). While the strong absorption (D) and shoulder (C) peaks represent dipole allowed 1s→4p transition and 1s→4p shake-down transition, respectively, the pre-edge peaks (A & B) represent dipole forbidden 1s→3d transition, indicating distorted octahedral symmetry of vanadyl molecular structure. The intensity of the pre-edge peaks is known to rise due to deviation of symmetry around the absorbing V center, allowing for stronger 3d→4p mixing. The sulfur K-edge XANES spectrum of pristine and soaked Nafion shows similar features, with one broad asymmetric peak (A) followed by shoulder type resonances (peaks B and C). The high intense broad peak A can be ascribed to an antibonding (C-S) σ^* MO of A1 symmetry, whereas peaks B and C represent (S-O) π bonding. It is evident that the soaked Nafion shows slightly reduced intensity for peaks B and C, indicating the possible change in S-O bond length of sulfonic sites due to interaction with vanadyl ions.

Predictive level understanding about chemical interaction between solvated cation and Nafion membranes is imperative for designing optimal membranes for all vanadium redox flow battery technology. The challenge is to employ efficient tools to probe the molecular level interaction inside the

PN15028/2703

nano-size pores of Nafion membranes. We used a combined experimental and theoretical analysis of core-level vanadium and sulfur K-edge spectroscopy to analyze possible chemical interactions such as solvent share, cis-, and trans-contact pair formation between solvated vanadyl ion and sulfonic sites of Nafion membranes. The density functional theory (DFT)-based energy calculation predicted both solvent share and contact pair interactions are probable. The time dependent-DFT calculated core-level vanadium and sulfur K-edge excitations for these chemical interactions were quite similar, and matches well with experimental spectra. This reveals that both contact pair and solvent share interactions between diffusing vanadyl ion and sulfonic sites of Nafion are probable as predicted by DFT calculations. However, the pore size, vanadyl ion concentration, electric field and temperature can greatly influence the energy barrier for contact pair and solvent share interactions and result in preference over other interaction. Additional detailed studies are warranted to gain quantitative view about these interactions and subsequently move to designing optimal membranes for redox flow batteries. Thus far, our project has yielded an invited talk, a focused workshop, and an invited article in a special issue of *Frontiers in Energy Research* focusing on energy storage devices.

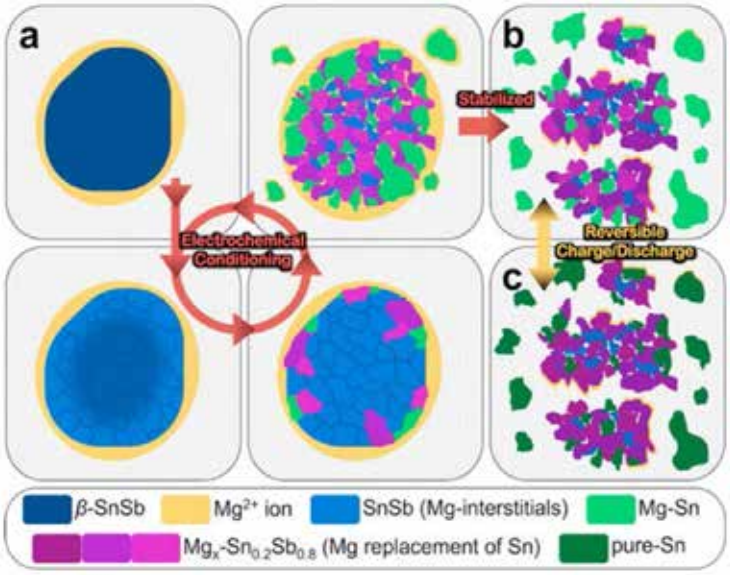
In FY 2016, we will collaborate with Lawrence Berkeley National Laboratory's Advanced Light Source (ALS) scientists to study the precise role of surface functional group of graphene materials using their developed *in operando* soft X-ray spectroscopy cell and *in situ* cells available to general users. Using engineered graphene with desired surface groups or dopant atoms, we will perform *in operando* carbon, oxygen, and nitrogen K-edge NEXAFS studies to identify bias-induced changes in their electronic structure. Analysis will provide insight into the structural changes that arise during charging/discharging and by extension the role of functional and dopant groups on graphene interfacial processes under realistic conditions.

Bridging Length Scales in Complex Oxides: From Point Defects to Defect Superstructures

Peter V. Sushko

We are providing a fundamental understanding of defect formation and interconversion mechanisms in multi-component materials, thus advancing materials modification by means of controlled defect processing.

Understanding defect behavior at high concentrations offers new opportunities for controlled synthesis of complex functional materials. The overall project objectives are to advance fundamental understanding of defects properties and their formation and inter-conversion mechanisms in multi-component materials, investigate the effects of their concentration using theoretical and computational methods, and identify the parameters affecting these interactions at several length scales. We are focused on ternary and quaternary materials and are considering examples pertinent to solar energy capture and conversion, electrochemical energy storage and ammonia synthesis. Our results describe the properties of complex solid solutions and offer mechanistic insights into optimal synthesis and processing pathways needed to harness these properties in practice.



Electrochemical Mg^{2+} insertion and extraction processes for a β-SnSb nanoparticle based on the TEM and DFT results: a) initial stage electrochemical conditioning; b) magnesiated Sn–Sb electrode stabilized after initial conditioning; c) No morphological or Sn–Sb compositional transformations occur during discharge; only changes in Mg content.

The high electron mobility of $SrTiO_3$ (STO) makes it an intriguing candidate for a wide range of applications. However, the usefulness of STO for solar applications is limited by its large optical band gap (3.2 eV) and propensity to form oxygen vacancies that undermine transport properties. We aspire to reduce the STO band gap without generating oxygen vacancies in the process. To this extent, we considered STO thin films doped with equal amounts of La and Cr, i.e., $Sr_{1-x}La_xTi_{1-x}Cr_xO_3$. Our results demonstrated that Cr and La associate at typical film deposition conditions and form quasi-1D chains. The Cr^{3+} ions at the Ti^{4+} sites lower the band gap by ~0.9 eV, while La^{3+} ions at the Sr^{2+} site provide electrostatic charge compensation, thus suppressing oxygen vacancies formation. Published in the American Chemical Society (ACS) journal *Chemistry of Materials*, this work reveals association mechanisms of intentional defects and suggests a path for imprinting quasi-1D wires in thin films.

Replacing Li^+ with a bivalent or trivalent ion is a promising route to improving storage capacity and energy density. Mg is an especially attractive alternative to Li due to its large specific capacity, small ionic radius, and high abundance. Transitioning from Li^+ to Mg^{2+} requires redesigning electrode and electrolyte materials. Sn is of great interest as a magnesium anode, having a high theoretical capacity, a small associated volume expansion, and a low Mg^{2+} diffusion barrier. We considered a promising electrode material, β-SnSb, and investigated the mechanisms of Mg incorporation and extraction using *ab initio* methods. Together with the experimental data obtained separately, these results allowed us to create a model for β-SnSb electrode evolution and predict optimal electrode structure as shown in the image. At the initial stages of intercalation, Mg occupies interstitial lattice sites. At higher concentrations, Mg displaces Sn from its lattice sites, leading to the formation of ~30 nm compositionally and functionally distinct particles: electrochemically active Mg-Sn and passive Mg-Sb alloys. These results, published in ACS's *Nano Letters*, point to nanostructured

PN14067/2651

Sn electrodes in the form of ~30 nm particles as a potentially optimal Sn electrode for Mg-ion batteries.

Novel approaches to efficient NH_3 synthesis at an ambient pressure are actively sought in order to enable production at compact facilities. The key is the development of a high performance catalyst that enhances dissociation of the N≡N bond, generally considered a rate-determining step. Prior research demonstrated that nano-structured oxide $[Ca_{24}Al_{28}O_{64}]^{4+} \cdot (e^-)_4$, denoted as C12A7:$e^-$, has a low work-function and can be used as an efficient electron donor. We examined how this property of C12A7:e^- enhances catalytic activity of nanoscale Ru. Using *ab initio* simulations, we established that electron transfer from the C12A7:e^- substrate to the supported Ru particles lowers the Ru work-function, promotes electron transfer to the adsorbed N_2 molecules and significantly reduces the dissociation energy of N_2. Further experimental studies demonstrated that with Ru/C12A7:e^- catalyst, the rate controlling step of NH_3 synthesis is not N_2 dissociation but the subsequent formation of N–Hn species. Thus, our results, which were published in *Nature Communications*, not only reveal the factors responsible for enhancement of catalytic activity but also redefine the bottleneck step in NH_3 synthesis reaction.

Controlled Synthesis of MOFs and Core-Shell MOF Composites

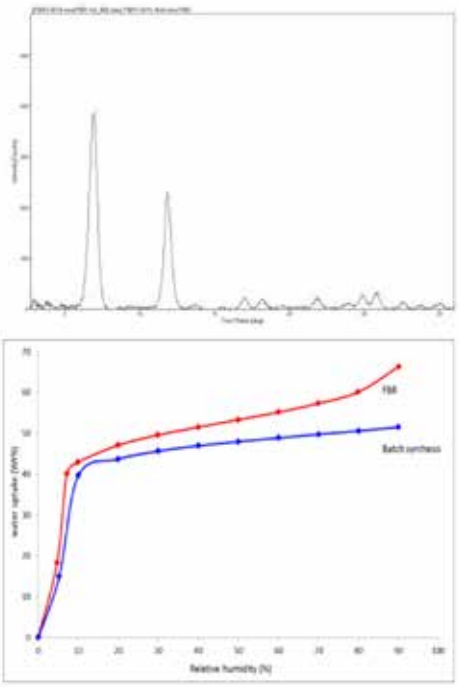
Radha K. Motkuri

We are developing a highly efficient process for metal-organic frameworks (MOFs) and composite synthesis, dramatically reducing production cost to make MOFs comparable to commercial sorbents.

In the past two decades, MOFs have attracted attention, in part owing to their enormous structural and chemical diversity that has made them superior to traditional porous materials. Despite this tremendous potential, the prospects for near-term deployment in commercial applications remain slim due to the lack of technologies and processes for synthesizing these materials in quantities and at costs that make industrial application feasible. The major challenges faced by the current batch processing approach include a lack of control over the product properties, scalability, the inability to extend the synthesis system to different reactants with similar structure, and results often in unwanted byproduct formation and low product yields. This project was designed to develop a novel advanced process for the continuous production of MOFs and MOF composites. This new approach represents a low-cost, fast, and easily scalable method that overcomes the previously mentioned difficulties/challenges associated with MOF production.

In continuation with the successful demonstration of evaporative aerosolization fluidized bed reactor (FBR) system for MOF synthesis, our primary focus in FY 2015 was to optimize the synthesis and particle size of one of the most important MOF structures that has superior performance in H_2O/fluorocarbons sorption studies (PNNL is currently using in its adsorption chiller applications). Next, we wished to attempt the synthesis of new MOF materials that have been either extremely difficult or have yet to be synthesized using the batch approach. Finally, we aimed to construct a new upgraded reactor to overcome the difficulties and improve the previous version to make the synthesis more efficient.

Using the upgraded reactor, we successfully demonstrated the synthesis of multiple MOFs. The optimization of the reactor temperatures, precursor injection rates, location of the spray nozzle, and aerosolizer operation were accomplished for NiMOF-74 and successfully synthesized by aerosolizing the mixture of nickel salt and organic linker in THF/water mixture at 130°C. The FBR is preheated at 125–150°C using heat tape with inlet nitrogen using inline heaters. At the end of MOF synthesis, the reactor temperature was raised to 150°C for 2 h for residual solvent removal and MOF product densification.



Top: PXRD pattern of NiMOF-74 synthesized using optimized conditions; bottom: enhanced water sorption capacities compare to the batch synthesis.

Mass measurements at the conclusion of the test resulted in the final Ni-MOF74 product that corresponds to a ~87% yield, with particle sizes in the required range of 100–300 µm. Thus, optimized material indicated enhanced water sorption characteristics compared with the batch synthesis material, as shown.

The FBR reactor further evaluated to the synthesis of new MOF materials that have been tough to prepare or need higher temperatures. To accommodate, the glass window of the reactor replaced with modified metal window and attempted synthesis for MgMOF-74 at 160°C, CrMIL-101 at 180°C and IRMOF-3 at 170°C. Our initial attempts showed the formation of MOF structure but with many impurities and unreacted starting materials that require further optimization.

To overcome difficulties in running the reactor continuously as well as deposition of the MOF product on the reactor walls and low rates of the MOF production, a new upgraded reactor was designed and constructed. This reactor design included a traditional atomization nozzle that can be inserted though the bottom of the reactor and the glass section was eliminated to allow the reactor to be heated up to temperatures of 225°C as shown. Further, the work generated a patent position, and application writing is in progress.

Newly constructed advanced all steel Gen4 reactor and new nozzle.

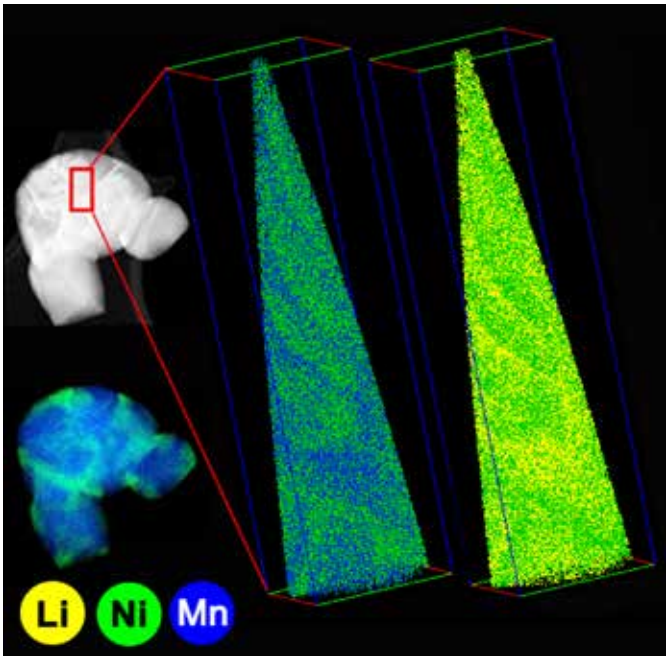
PN15056/2731

Developing Next-Generation Multimodal Chemical Imaging Capability by Combining STEM/APT/STXM/HIM

Arun Devaraj

We are developing a common analysis platform for integrating multiple microscopies to characterize commercially viable catalyst materials supported on porous metal oxides and energy storage materials.

Complex materials relevant for energy and environmental applications undergo a dynamic transformation during their life-cycle critical to understand and assess structure-property relationships accurately. For example, to develop next generation energy storage capabilities, the mechanism of degradation of current state-of-the-art high performance electrode materials during repeated charge-discharge battery cycling must be understood for suitable microstructural modifications can be adjusted through innovative designs of new electrode materials. For environmentally relevant materials, it is important to understand the influence of nanoscale structure and composition of natural and anthropogenic atmospheric aerosols on global climate because of their impact on precipitation and snowfall as ice and cloud condensation nuclei. To address these needs, we employed multi-modal chemical imaging capability and computational simulations to understand the structure, composition, and chemical state correlated with material behavior.



By using APT, the 3D distribution of Li and its correlation with Ni, Mn, and O can be quantified in advanced Li-ion battery cathodes both before and after cycling.

Through our a multi-modal approach, we are attempting to understand the nanoscale structure, composition, and chemical state of elements in sodium (Na)- and lithium (Li)-ion battery cathode materials as functions of different synthesis conditions at different stages of electrochemical cycling. This information will aid not only in the fundamental scientific understanding of starting microstructure and degradation of microstructure with electrochemical cycling but will also help to improve synthesis conditions and possible development of protective coatings and other methods to prevent battery capacity fading during long-term charge-discharge cycles. A similar characterization approach was used for the nanostructure and chemistry of atmospheric aerosols.

Continuing from previous fiscal years, the first set of experiments for using multimodal chemical imaging to understand the nanoscale structure, chemistry, and chemical state of mineral dust atmospheric aerosols, we completed a study that was published in *Geophysical Research Letters* about the dependency of ice nucleation property of volcanic dust with its crystalline nature. We have a second publication on ice nucleation versus the structure, composition, and chemical state of H_2SO_4-coated kaolinite before and after washing that is currently being prepared for submission to a high impact journal. In addition, continuing the collaboration with beam line scientists at Advanced Light Source at Lawrence Berkeley National Laboratory, we conducted a first set of experiments for developing *in situ* scanning transmission X-ray microscopy (STXM) liquid cell holder to study the lithiation of silicon nanowires that are candidate anode materials for next generation Li-ion batteries.

Another significant effort during FY 2015 was publishing the key results obtained on Li-ion battery materials by atom probe tomography (APT). We successfully achieved the 3D nanoscale visualization of Li-ion segregation in both pristine and cycled $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

PN13033/2514

cathode materials. The results were compared to the APT results with rather uniform Li distribution in $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathode materials. Additionally, APT results were correlated with scanning transmission electron microscopy (STEM) energy dispersive spectroscopy measurements to establish the strength of APT in quantitatively probing the distribution of light elements like Li in addition to the transition metals. This paper was published in *Nature Communications* and is depicted visually in the accompanying figure.

Further developing PNNL computational capabilities using level set simulations to understand field evaporation of heterogeneous materials in atom probe tomography, we published a level-set method on the finite element method with collaborators from Cameca Instruments in *Computer Physics Communications*. A second paper on comparing experimental APT results of CeO_2/ZrO_2 oxide multilayer grown by molecular beam epitaxy with simulated APT results of the same structure was published in Applied Physics Letters. In this work, we demonstrated the capability to conduct computationally guided APT of complex composite materials like oxide multilayers that have a wide range of applications.

Development of Hierarchical Porous Structured Materials for Energy Storage Applications

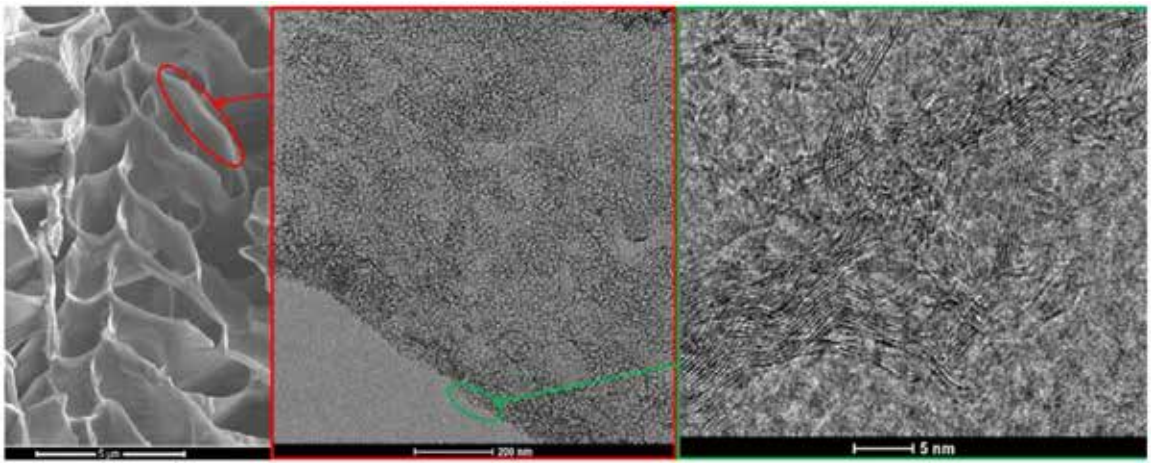
Luis Estevez

We are developing novel porous materials with tailorable properties to target specific prerequisites of certain electrodes for energy storage applications, specifically lithium ion battery (LIB) anodes and supercapacitor electrodes.

The U.S. transportation sector is overwhelmingly powered by the internal combustion engine (ICE). This results in roughly one quarter of our total energy use to be in the form of petroleum. Not only does the use of this fossil fuel have detrimental environmental effects, but it is coincidently similar to the amount of petroleum we import each year. Thus, there has been a great demand for a move toward an electric vehicle (EV) powered fleet, particularly as petroleum becomes more scarce. A major impediment to this goal is the fact that the current energy storage technology of choice for EVs, the LIB, is roughly an order of magnitude away in terms of energy density and at least that, in terms of power density. To bridge these gaps, we are advancing two distinct energy storage technologies that can be used in an EV and potentially in a hybrid EV: supercapacitors and silicon-based LIBs.

Supercapacitors electrodes. Supercapacitors (SCs) are one of the few energy storage technologies that can compete with the high power densities present in an ICE (~1–10 kW/kg for either system). Unfortunately, the most common SCs, electric double layer capacitors (EDLCs), muster energy densities only at least two orders of magnitude below ICEs (typically 1–10 Wh/kg for SCs and >1000 Wh/kg for an ICE). Because the mechanism for energy storage in an EDLC is the adsorption of ions present in the electrolyte onto the electrode surface, high surface area electrodes are typically employed with specific surface area (SSA) values typically greater than 1500 m^2/g. The most common SC electrodes are usually activated carbons that are electrically conductive and meet the large surface area prerequisite through an extensive network of small nanometer (< 5 nm) sized pores. The problem is that these commercially activated carbons often have a ramified porous structure that can give rise to kinetic barriers for faster moving ions, reducing SC power density to increase energy density.

We synthesized a hierarchical porous carbon (HPC) materials platform with controllable porosity in the three porosity length scales (as designated by IUPAC): micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) by using three different mechanisms: CO_2 activation, hard colloidal templating, and ice templating, respectively. This process enabled our HPC materials to have an interconnected vascular-like network of larger macro/mesopores leading into smaller micropores. The open structure will enable the HPCs to be maximized for both power density and energy density by using the interconnected mesoporous network to mitigate kinetic barriers for ion conduction to high surface area sorption sites. Additionally, we exploited the ability to synthesize both extensive micropores and larger meso/macropores to fabricate HPCs with both high SSA and large amounts of



Left: The hierarchical structure apparent in the HPC-G materials by way of the large macropores; middle: macroporous walls consisting of smaller mesopores; right: a higher magnification TEM image of smaller mesopores, revealing the graphitic nature of the mesopores present in the material.

PN15004/2679

void space, typically measured as pore volume, with space necessary for loading transition metal oxides into the larger mesopores, adding pseudocapacitance from the high SSA micropores. Finally, we explored alternative HPC materials that are more graphitic but have the same tunable morphology combined with large SSA and pore volume characteristics.

Using the triple templating synthesis strategy, we synthesized HPC materials with varying surface areas, pore volumes, and pore size distributions. Highlights include HPC materials with a large SSA of over 2800 m^2/g combined with colossally large pore volumes of over 10 cm^3/g. For mesoporous carbons, it is considered high to have pore volumes over 5 cm^3/g, a number we easily eclipsed. In fact, we cannot find any nanoporous carbons in the literature with the combination of these values. We synthesized additional batches of the large SSA/pore volume HPCs and found the results repeatable to within 5–10%. Attempts to fabricate these extremely porous HPCs into electrodes for EDLCs have proven difficult due to their outstanding textural properties, but samples were sent to collaborators at Florida State University for testing as lithium ion capacitors (LICs), hybrid energy storage devices with an LIB anode and EDLC electrode as cathode. Using a typical lithium salt in an organic LIB electrolyte, our HPC material showed promising initial results of ~107 F/g and energy density of ~55 Wh/kg based on the active HPC material. Further, cyclic performance was excellent with little capacity fading even after 10,000 cycles. We anticipate that our efforts to fabricate more graphitic and electrically conducting HPC materials will increase these results. Future work with these carbon systems include *in situ* growth and loading of MnO_2 nanoparticles into large pore volumes and subsequent testing as SC electrodes.

Silicon-based LIB anode. While SCs can help bridge the ICE gap in terms of specific power, employing a silicon-based anode in a LIB is one way to bridge the gap for energy density. Silicon has over 10 times the theoretical capacity of graphite, but the major impediment to its use as a battery electrode is that the Si anode pulverizes and breaks apart during the charge-discharge cycling. Previous work at PNNL has demonstrated how porous silicon can mitigate this pulverization by allowing the silicon to expand within the void space; other researchers have found that smaller silicon particle sizes can mitigate the pulverization. We combined both approaches to synthesize composite silicon-graphite oxide materials. We employed a hierarchical porous silica ($HPSiO_2$) material that we functionalized and attached to suitably functionalized graphene oxide (GO) nanoplatelets. Both the silica and GO can later be reduced to silicon and reduced GO (r-GO) and assembled into LIB anodes. An alternative strategy was also used, whereby silicon nanoparticles oxidized a thin (<5 nm) layer of silica that can be functionalized in a manner similar to the $HPSiO_2$, attached to the GO, and easily reduced for assembly into an LIB anode. This alternative strategy forgoes the magnesiothermic reduction route typically employed to reduce the silica. Lastly, these silicon-silica core-shell nanoparticles (CSNPs) were functionalized with a plan to load the CSNPs into HPC materials. Being a hard carbon material, the HPCs can be used as a LIB anode in their own right, but our plan was to use this initial capacity inherent in the HPCs and increase it via the addition of the CSNPs.

Initial results in attaching the $HPSiO_2$ and CSNPs to the GO nanoplatelets look promising via SEM and TEM characterization; we are also using XPS and FTIR to elucidate the nature of the attachment. Additionally, we used our considerable experience from another project to synthesize HPCs with larger pores in the small macropore range (100–500 nm). Thus far, we have fabricated pores in the 50–100 nm range, but we are optimizing the synthesis to get larger pores. We initially tested these HPCs without loaded CSNPs and found interesting results. After the SEI layer is formed on the HPC anode, the HPC discharge capacity at lower C rates is comparable to what is typically observed for graphite (~280 and ~270 mAh/g, respectively). At higher rates such as 1C, our HPC anode was still at a discharge capacity of ~250 mAh/g. At a very high discharge current of 1.2 A/g (4C), the capacity was still above 200 mAh/g for our HPC anode. These capacities at higher discharge rates compare favorably to standard graphite LIB anodes. From these initial results, we expect to optimize the HPC during FY 2016 until we find the best scaffold to load with the CSNPs.

Our next steps in FY 2016 involve leveraging the considerable capabilities of PNNL's research in transportation energy storage to develop and characterize the electrochemical performance of these novel materials. Additionally, we will maximize other potential applications for porous materials by working with internal projects on gas adsorption, catalyst supports, and alternative energy storage. One project of particular note involves the functionalization of porous carbon materials for use as vanadium redox flow batteries. The collective results of this work has yielded completion of a manuscript for journal submittal as of FY 2015 end.

PN15004/2679

Development of Viologen Based Ultra-low Cost and High Performance Aqueous Redox Flow Batteries

Wei Wang

We are developing low-cost materials as energy-bearing redox for redox flow batteries (RFBs) as a critical energy storage component of the future electric grid to improve transmission and distribution efficiencies and integrate renewables, thus lowering electricity cost and reducing greenhouse gas emissions.

Increasingly, RFBs are being recognized as the most promising candidate for large-scale energy storage due to their unique advantages. Among the various RFB technologies, vanadium based flow batteries (VRBs) are currently the most widely used system. However, the cost of VRB is high due to the expensive vanadium element. We previous developed methyl viologen (MV)-iron (Fe) flow battery based on low cost MV and iron materials that unfortunately encountered a stability issue on the iron electrolyte. In this project, we are identifying and developing a new redox flow battery based on MV and hydro-TEMPO materials, both of which are earth abundant elements, sustainable, and low cost in large-scale production, critical to achieve an overall cost reduction of the flow battery system. Our goal is to develop the flow battery based on these low-cost redox materials, a scenario that has great potential to reach DOE's long-term goal for stationary energy storage.

We successfully developed a total organic aqueous redox flow battery (OARFB) using low-cost and sustainable MV (anolyte) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-HO-TEMPO, catholyte), and benign NaCl supporting electrolyte. The electrochemical properties of the organic redox active materials were studied using cyclic voltammetry and rotating disk electrode voltammetry. Based on these studies, it was determined that the diffusion coefficients and the redox reaction constants of both compounds are several times higher than those of the inorganic redox compounds adopted in acidic aqueous flow batteries such as vanadium and iron. The excellent transport and kinetic properties of these compounds also indicate that the system can be developed at a high power operation, further reducing the system cost.

The MV/4-HO-TEMPO ARFB has an exceptionally high cell voltage at 1.25 V, which is higher than those of the currently reported aqueous redox flow batteries using organic redox couples, translating to fewer cells required for rated power. Flow cell tests with these two compounds have been performed at two different concentrations, 0.1 M and 0.5 M with NaCl as supporting electrolyte. The flow cell tests demonstrate the new system can be operated at high current densities ranging from 20 to 100 mA/cm2 and deliver stable capacity for 100 cycles with nearly 100% coulombic efficiency and rather stable cyclic capacity.

In comparison to the reported organic ARFBs based on quinonoid compounds, the advantages of the MV/4-HO-TEMPO ARFB include higher energy density, comparable or exceeding current density, longer cycling performance, benign electrolytes, and lower membrane cost. The overall technical merits of MV/4-HO-TEMPO are very attractive for further technical development. In addition, these organic compounds consist of earth abundant elements hydrogen, carbon, nitrogen, and oxygen, are sustainable and low cost, and are available in existing large-scale production. In addition, they allow the use of cheaper anion exchange membranes than Nafion membranes used in acidic media. Cost estimation suggests the MV/4-HO-TEMPO ARFB is lower than $180/kWh versus $447/kWh for state-of-the-art VRB owing mainly to the cost reduction on the chemicals, which approaches DOE's cost target on large-scale energy storage of $150/kWh.

In summary, the MV/4-HO-TEMPO ARFB displays attractive technical merits and thus represents a major advance in ARFBs. Future research will be focused on striving to gain an understanding of the capacity decay mechanism and molecular structure modification to achieve even greater solubility.

PN15058/2733

Directed Mesoscale Synthesis of Tunnel Structured Materials for Energy Applications

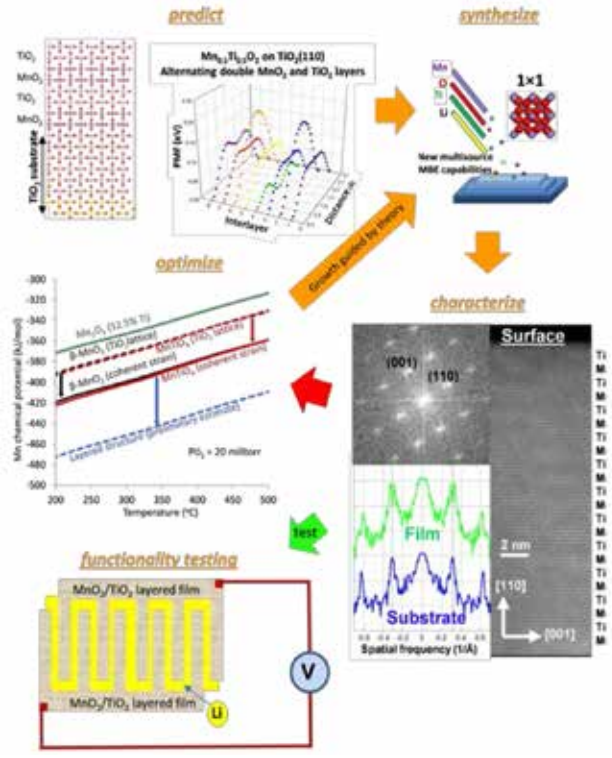
Eugene S. Ilton

The rational design of materials with properties optimized for energy applications is vital to a sustainable future. At its most fundamental level, we are using theory in this project to design materials with interesting properties relevant to energy storage and conversion.

For this project, we are melding experiment with theory to provide a predictive capability, forming the basis for the rational design of materials, specifically epitaxial films, with interesting properties. Progress to date shows that we are on track to help position PNNL for anticipated emphasis on integrated theoretical modeling and experimental research for predictive design of functional materials. A general result thus far is the demonstration that the synthesis of epitaxial thin-films, explicitly called out in DOE workshops on Mesoscale Science as examples of designed and self-organized systems, can be guided by theoretical predictions. In fact, we are approaching this goal from two directions: predicting films with interesting properties and then making them, and using *ab initio* thermodynamics to place the results in context and provide guidance to future synthesis.

The specific materials of interest are tunnel structured Mn/Ti oxides that are intrinsically mesoscale in spatial and compositional dimensions crucial in technological applications. However, the complexity and poor quality of natural, hydrothermal, and electrochemically synthesized Mn/Ti oxides have hindered efforts to understand their fundamental structure-property relationships and thus often prevent reaching their full technological potential. To address this issue, we are using molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) to make high-quality epitaxial $Mn_xTi_{1-x}O_2$ single-crystal films for characterization and experimentation in conjunction with computational modeling. Our interest in mixing Mn/Ti stems from our measurements which have shown that Mn lowers the band gap of rutile (TiO_2), whereas Ti increases the thermal stability of MnO_2.

Earlier results integrated over FY 2013 and FY 2014 on the successful synthesis of homogeneous single-crystal (001) and (110) oriented $Mn_xTi_{1-x}O_2$ rutile-structure films have been published. This work highlighted the limits of Mn/Ti mixing as function of film thickness, success in expressing the unstable (001) face which provides high surface area access to the 1×1 tunnels, and the usefulness of *ab initio* thermodynamics to explain film stability as a function of growth conditions and Mn/Ti composition. The published *ab initio* thermodynamic model included compositional and bulk lattice strain effects as well as temperature and O_2 pressure. Since then, we have added the effects of surface energy, coherent strain to the substrate, Mn and Ti distribution, and oxygen vacancies. Importantly, segregation of Mn and Ti yields more stable films which motivated our efforts making MnO_2 and TiO_2 layered films. Atomistic models of mesoscale Li diffusion in Mn/Ti tunnel-structured materials have also been published. Specifically, atomistic modeling showed that alternating cation rows containing only Ti or Mn greatly lowered the activation energy for Li diffusion relative to bulk structures where Mn and Ti were homogeneously mixed. In other words, a compositionally layered structure should perform better than one with a perfect solid solution.



Theory used both to guide synthesis and predict compositions and Mn-Ti distributions of $Mn_xTi_{1-x}O_2$ films.

Subsequently, we modeled Li diffusion in films that have been coherently strained to the substrate, which constitutes a first. Coherent strain is predicted to increase the activation energy for Li diffusion in a

PN13004/2485

pure MnO_2 film. However, layering of MnO_2 and TiO_2 offsets this effect to some degree while also increasing the electron conductivity. In fact, where Li diffusion is predicted to be faster in the larger TiO_2 tunnels, electron transport is more facile through the MnO_2 layers. Thus, the MnO_2 and TiO_2 layers display synergy and both sets of calculations suggest the advantage of layered structures.

The above process illustrates our goal of rational design. As described above and in the figure, we used theory to guide synthesis and predict compositions and Mn-Ti distributions of $Mn_xTi_{1-x}O_2$ films that should significantly facilitate Li diffusion in the tunnels while promoting electron conductivity. Given this incentive, we made layered films. Whereas e^- conductivity was high (four-point probe test), the three-electrode test indicated low Li intercalation; thus, we fabricated MnO_2/TiO_2 layered islands of nanometer height and micron width on the TiO_2 (110) surface by epitaxial deposition through physical masks to increase the (001) surface area and potential access of the tunnels to Li. Li intercalation was still poor, and it became apparent that the three-electrode test was inappropriate, plus we could not design a film that could be adequately tested with this method. We now have a redesign in which the layered films form an interdigitated configuration: Li° will be deposited in the central portion via MBE with a protective layer deposited on top and electrodes attached. Testing will occur in FY 2016 under the auspices of another project.

This combination of theory and experiment provides a powerful methodology for exploring intrinsic structure-property relationships for predicting and then synthesizing thin films with promising properties for energy applications. We are particularly pleased that our results and methodologies developed have been incorporated into a DOE proposal. In addition, our success predicting that MnO_2 thin films can be stabilized by layering with TiO_2 films and then synthesizing the material will be used as a relevant example in an Early Career Award proposal.

Enabling Sodium Batteries with Advanced Electrolytes

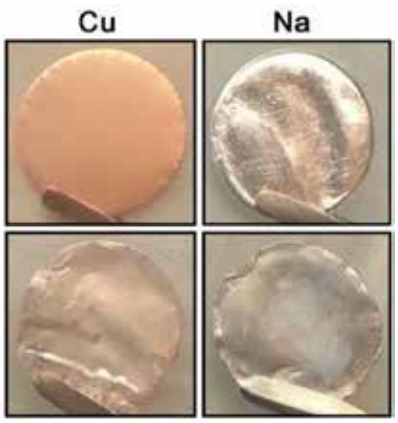
Jason Zhang

This project demonstrates the viability of solid sodium (Na) metal-based batteries that operate at or near ambient temperature based on low cost earth-abundant materials.

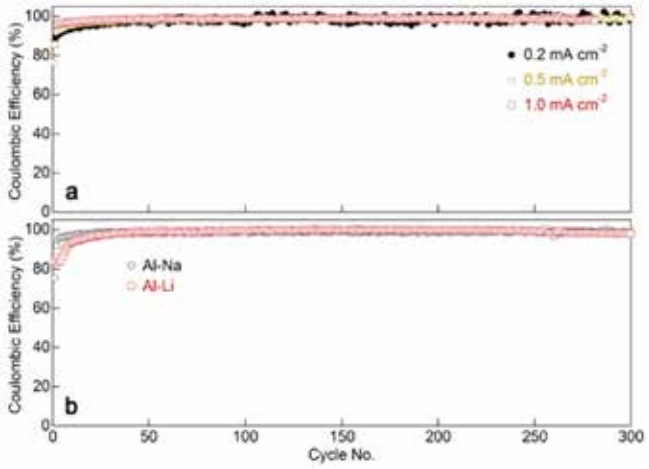
Commercial Na metal batteries (i.e., Na-S or Na-$NiCl_2$ [ZEBRA] batteries) employ high temperatures (> 300°C) in which the metal is molten liquid with a solid ceramic electrolyte. Operation at high temperature, however, complicates the materials selection, operating system complexity, and hazards associated with large batteries. There has been significant interest in recent years in Na-ion batteries in which Na^+ cations are intercalated into carbon or form alloys similar to Li-ion batteries, but the lower capacity of sodium relative to lithium due to its higher mass limits the energy density obtainable from such batteries, which have relatively expensive manufacturing costs compared to Li-ion. Thus, to maximize the energy density and power capability of battery chemistries based on Na^+ cations requires the direct use of Na metal as an anode. Another difficulty has arisen, however, by battery researchers/developers from the instability of Na metal in conventional electrolytes. The focus of this project, therefore, is the demonstration of new electrolytes that permit the preparation and extensive cycling of full Na|cathode cells for ambient temperature usage, which will be the key to the implementation of practical cell chemistries for commercial low-cost Na batteries, especially those well suited for grid-scale energy storage.

The cost of NaFSI salt used in the electrolyte is high, which restricts the commercial viability of this cell chemistry. Although no other electrolytes were identified that cycled as well as those with NaFSI when it was fully replaced with another sodium salt, electrolyte formulations with mixed salts in which a significant fraction of the NaFSI was substituted with a second salt did cycle well with high Coulombic efficiency. Despite the high cost of Cu (contributing significantly to the overall cell cost), mass Li metal is typically plated on a Cu metal current anode collector because Li does not alloy with Cu but does with Al metal. The latter metal, however, is both significantly less expensive and has a substantially lower mass than Cu. In contrast with the Li metal, Na metal does not alloy with either Cu or Al. An equivalent highly efficient cycling of the Na metal was demonstrated on both Cu and Al current collectors, indicating that low-cost Al may be used as the anode current collector for Na|cathode batteries.

Testing of electrolytes in a full cell configuration with a Prussian White (i.e., $Na_{2-x}Fe_2(CN)_6$) cathode resulted in a poor cycling performance. Subsequent testing indicated that one probable cause for this is the instability of the electrolyte with the cathode's Al metal current collector. Cyclic voltammetry measurements indicated that significant Al corrosion occurred when the electrolyte was cycled with an Al working electrode at high potential. The scientific literature for LiFSI electrolytes indicates that this is due to a chlorine impurity in the salt from the synthesis procedure that is difficult to remove. A variety of methods were employed using various additives to passivate the Al current collector when cycled with this electrolyte, but with mixed success. Poor cell cycling may also be from limited stability at high potential of the ether solvents employed for the electrolytes. A wide range of other solvents were tested that are expected to have improved oxidative stability, but these resulted in poor Na metal plating/stripping.



Optical images of the Cu (working) and Na (counter) electrodes: (top) new and (bottom) after first cycle plating of Na metal on the Cu current collector.



Coulombic efficiency for the cycling of (a) Cu|Na (at different rates) and (b) Al|Na cells (at a 1.0 mA cm^{-2} rate), verifying the exceptionally high stability of the electrolyte for the plating/stripping of solid Na metal.

To obtain additional information and further scrutinize the performance of full cells, ongoing work includes the testing of full Na|cathode cells in which the Prussian White cathode active material being replaced with $Na_{0.44}MnO_2$ with either Al or carbon as the current collector.

PN15093/2768

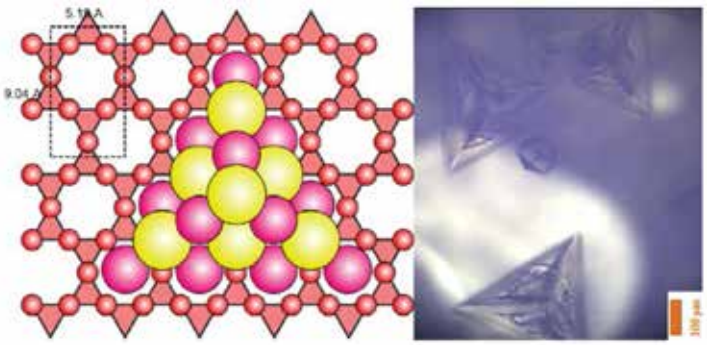
Fundamental Mechanisms of Nucleation and Growth of Particles in Solution

Marcel D. Baer

This work will provide the necessary theoretical framework and simulation tools that enable an understanding of the microscopic principles of nucleation, growth, and self-assembly.

Inorganic polymeric form a large class of materials ranging from sol-gel networks to metastable zeolites and hybrid metal-organic framework materials. The synthesis and use of these highly engineered systems has evolved over the past 100 years from "black magic" into at least a technical art. The next step—the one that approaches modern science—requires the continued development and application of a gamut of synthetic methods, illustrative model systems, characterization techniques, and interpretation via computation and simulation that can bridge from quantum mechanics through fluid and structural mechanics.

We want to understand the growth kinetics of size selective molecular clusters that form the secondary building blocks of polymeric inorganic networks in a joint experimental and theoretical effort. Thus, our focus in this project is on the use of molecular models to mimic and understand the underlying principles of how surface assembly of inorganic oxide supports their related surface-grafted organometallic fragments. To this end, this project is developing new research capabilities for the simulation of reactivity and structure in complex heterogeneous and homogeneous environments, establishing a theoretical framework, and using simulation tools to understand the microscopic principles of nucleation.



Schematic of potential RbI pyramid on mica surface (left) and optical image of rubidium iodide crystals growing from supersaturated aqueous solution.

In FY 2015, we continued with the experimental focus of understanding on how silica particles nucleate and grow from monomeric silane species. We used a solution-based acid catalyzed hydrolysis reaction to grow octameric polyhedral oligomeric silsequioxane (POSS) starting from a monomeric $R`Si(OR)_3$. We monitored the reaction progress as a function of temperature and pH during the assembly process utilizing mass spectroscopy and solution phase ^{29}Si NMR to identify intermediate oligomers that were formed during the process. Our results showed that we formed significant amounts of tetrameric species with small amounts of octameric, decameric, and dodecameric species; however, almost no dimeric species were seen during the growth process.

A new project was started to test the hypothesis that according to the theories of nucleation, a population of transient alkali halide clusters may exist on the mica surface prior to nucleation. We used fast-scanning AFM to investigate the existence and behavior of such small alkali halide clusters, ideally characterizing both their populations and lifetimes. Because the concentration of such clusters is directly related to their free energy of formation, this approach can provide an alternative route establishing the free energy landscape for nucleation. Thus far, the controlled growth of microscopic crystals was shown for RbI on mica.

The theoretical effort in FY 2015 was focused on ion-pairing as the first step of nucleation and growth for calcium carbonate in the high dilution limit. We used state-of-the-art *ab initio* density functional theory (DFT) and classical force fields (FF) representations of interaction to obtain condensed phase PMFs. This process allowed us to coarse-grain the ion-ion interaction to study the nucleation of small clusters and their free-energetics using dynamical nucleation theory. Primarily results using the AVBMC method show significant differences for both models for the nucleation.

During FY 2016, we are interested in extending the POSS studies to look at microscopic tools, particularly cryo-transmission electron microscopy, to study particle growth. We will develop a kinetic model of the growth process and study the effect of pH on growth kinetics. The $CaCO_3$ affords a more direct connection to Classical Nucleation Theory, which has been a successful and widely used theory to predict nucleation rates. In addition, we will use the *ab inito* PMFs of ion-pairing to coarse-grain the ion-ion interaction in the condensed phase and study the nucleation of small clusters and their free-energetics using dynamical nucleation theory. The nucleation of alkali halides will be studied with fast-scanning AFM in the low dilute limit and in parallel simulations will investigate ion distribution on idealized mica surfaces.

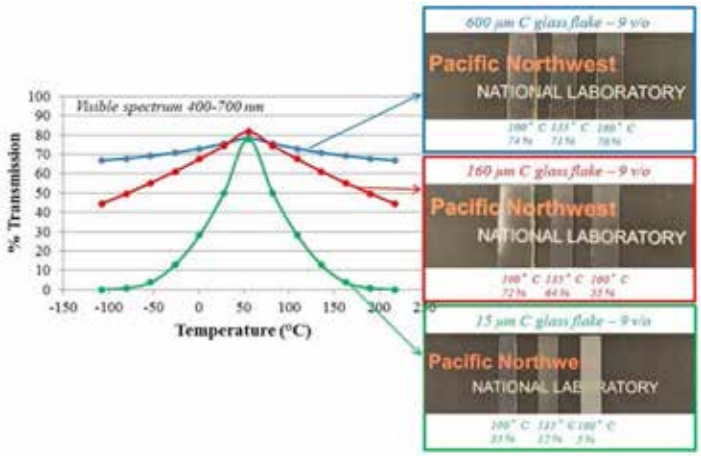
PN14025/2609

High Aspect Ratio Functional Composites for Thermal Optical Applications

David M. Reed

We are developing novel composite structures that will change reversibly from transparent (or any underlying color) to opaque in a targeted temperature range. Innovative design strategies are employed to fabricate inexpensive functional materials for applications in the energy management of buildings, vehicles, and consumer markets.

Composite materials have been used extensively in electronics, optics, and structural material application sectors because resident collective properties are often unique and not found in single-phase materials. Transparent structural composites (i.e., glass fiber-loaded polymers), however, are limited applications because of their tendency to have a narrow temperature window in which they are transparent. With changes in temperature, these composites become opaque due to refractive index mismatch accompanied by interfacial light scattering. The refractive index variation of polymeric materials with temperature ($d\eta/dT$) is often one or two orders of magnitude higher than for inorganic glasses. Over a small temperature range where refractive indices are matched, the composite will remain transparent. Methods have been employed to achieve this effect (thermochromic pigments, electrochromics, and meta-materials), but their use is limited by their high cost.



The ability of the smart membranes to change reflectivity can render the composite either an active cooling or heating component due to environmental changes.

For this project, optical grade polymers were selected based on refractive index match to standard compositions, namely E and C glasses. The refractive indices were measured on the glass fillers and polymer matrices as a function of temperature using the Becke line technique and the prism coupler method developed at PNNL. During FY 2014, we focused on thermosetting epoxy systems because of their availability and ease to fabricate into films. The E and C glasses chosen offered a wide range of morphologies and aspect ratios (e.g., particulate, fiber, and flake). An index-matched composite with controlled microstructural features of the filler phase provided a path to realize a composite that could reversibly change from transparent to opaque with temperature. The filler aspect ratio and temperature dependence of the polymer refractive index are two important parameters that determined the breadth of the transparent window and width of the temperature window in which the composite transitions from transparent to opaque, respectively. Manipulating the morphology and chemistry of the composite would allow a tailoring of the thermo-optical response over a broad temperature range.

The thermosetting epoxy resin system from DOW® Chemical is widely available with various catalysts and diluents that can be added to change the crosslinking density and resulting molecular structure. These additives give the ability to tailor the refractive index and therefore match the glass filler at different temperatures. Significant progress was made on improving the refractive index characterization technique as a function of temperature and was instrumental in providing the ability to measure a broad range of polymers in a timely manner.

Also during FY 2015, we successfully fabricated composites based on the epoxy and glass flake system developed in the previous year that reversibly change from transparent to opaque with increasing temperature. We additionally demonstrated that the transition from transparent to opaque can be controlled through the proper selection of filler aspect ratio and matrix. As the epoxy-glass flake system has been fundamental in providing a basic understanding of the microstructure-property relations in composites, our findings were used to fabricated composites with optical grade thermoplastics with improved durability. Trends observed in the epoxy system have also been verified for thermoplastic systems, and composite optical properties have been predicted through modeling and show good correlation to experimentally derived results.

Our work in FY 2016 will focus on fabricating matrix materials with a greater negative $d\eta/dT$ (or greater thermal expansion coefficient α) and improved durability to allow the reversible switching window from transparent to opaque to occur over a smaller temperature range. Surface modification of the filler phase will also be examined to improve both wetting at the interface and optical response of the composite.

PN14019/2603

High Information Content Polymers and Their Assembly into Structural Motifs

Chun-Long Chen

We are developing high-information content polymers to understand their self-assembly into higher order structural motifs, an ability that will ultimately enable biomimetic functional materials.

High-information content polymers will mimic the ability of proteins and peptides to exhibit secondary and tertiary structure as well as self-assemble into oligomeric complexes and extended ordered matrices. The self-assembled materials developed in this project can perform functions beyond protein- and peptide-based materials. This work will lead to an understanding of the assembly and thermodynamic and kinetic controls on those pathways, the rates at which assembly occurs, and the degree of order in the final structures. In short, we seek to create a scalable, robust approach to synthetic high information content polymers with sophisticated functions; use powerful methods of investigating self-assembly to develop a fundamental understanding of assembly in the synthetic systems; and integrate polymer synthesis, characterization, and theoretical modeling to create a true predictive science of synthesis for high information content polymeric materials.

In FY 2014, we designed and synthesized two types of sequence-defined polymer sequences for self-assembly of highly ordered materials. We tuned the peptoid self-assembly chemical characteristics rationally, and we observed that a slight change of sequence design caused dramatic differences in polymer self-assembly. The first designed class of synthetic polymers contained an architecture that did not involve peptide bonds. Using R-group substituted monomers, we performed batch synthesis of homopolymers, solution-phase synthesis by addition of one monomer at a time using deprotection steps, and a solid-phase method using a submonomer approach to create polymers by extending the chain a fraction of a monomer at time. Our other modeled class of synthetic sequence-defined polymers informed experimental designs structurally. In the simulations, it was determined that imine sidechains increased helical propensity and chiral linkers increased conformational order.

In FY 2015, we synthesized over 10 three-fold peptoids and investigated their self-assembly into porous networks. Adding reversible chemical bonds into the design, we demonstrated that self-assembled peptoid materials exhibited reversible structural changes in responding to pH. We also synthesized over 20 membrane-forming peptoids and demonstrated that attaching functional groups at arbitrary locations in the peptoid sequence leaves the basic membrane structure intact. Under dry conditions, atomic force microscopy (AFM) results show that these free-standing peptoid membranes exhibit a thickness of 3.5–4.0 nm, and analyses via X-ray diffraction (XRD) determined that they are highly crystalline. Transmission electron microscopy (TEM) results showed that they also contain well-aligned strips of flexible carboxylate groups. Based on these AFM, XRD, and TEM results, we generated a proposed structural model for peptoid membranes. Molecular dynamics were used to confirm the model and understand the interactions leading to a robust peptoid assembly. Simulated structures showed that extensive π-stacking in the hydrophobic region and disorder in the carboxyl tails. In addition, simulated XRD data is in good agreement with the experimental data, and the formation of well-aligned strips of disordered hydrophilic domains agree well with TEM data. Molecular simulation further confirmed that peptoids packed anisotropically to form membranes.

By exposing peptoid membranes to a range of solvents and high temperature, we demonstrated that they are highly stable. For example, *in situ* AFM studies showed that no significant disruption was observed when they were placed in a mixture of water and organic solvents, or even in pure CH_3CN and EtOH for over 6 hours. Similar to lipid-bilayer membranes, *in situ* AFM results demonstrated that peptoid membrane exhibited salt-induced thickness changes. By exposing the materials to NaCl solution or PBS buffers of increasing concentration, we observed thickness changes from ~4.2–5.4 nm. We also demonstrated that peptoid membranes could coat surfaces in single-layers through a two-step heterogeneous nucleation process. Moreover, they exhibited anisotropic self-repair.

During FY 2016, we will investigate designs that incorporate specific sidechains that drive formation of functional pores and use sidechain diversity to provide ion-selectivity of peptoid membranes and porous networks for molecular separations. We will continue using *in situ* AFM to characterize the dynamics of peptoid assembly and investigate the difference in the pathways of assembly and the thermodynamic and kinetic parameters among different peptoids. With the help of molecular simulation, we will ultimately understand how polymer length, sequence, and chemistry affect the assembly pathways and the thermodynamic and kinetic parameters that will therefore enable a rational design of biomimetic functional materials with tunable structures and functionalities.

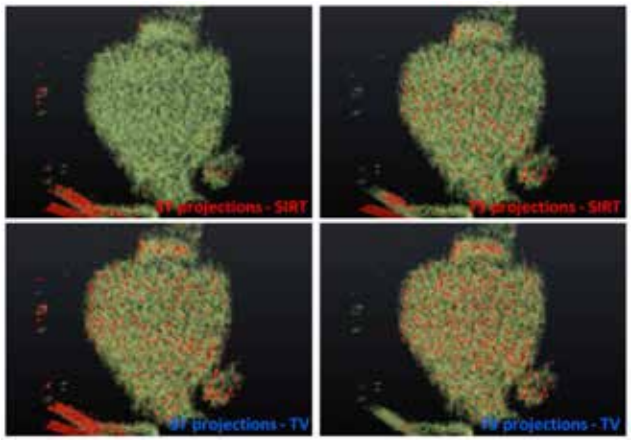
PN14012/2596

High Resolution and 3D Imaging of Nanomaterials

Ilke Arslan

Advances in technology are often linked to advances in methods for characterization. This project aims to advance characterization methods to provide input for the rational design of next generation materials.

We are advancing and combining nanoscale techniques to further complex materials examination. One such set of complex materials is catalysts/zeolites. The characterization-synthesis loop is an important aspect of designing and controllably synthesizing a material of industrial significance. Likewise, characterization on the atomic and nano scales allows for a fundamental understanding of the catalytic processes that aids in designing a better catalyst. Another set of complex materials is biological materials. Both zeolites and biological materials are non-conductive, electron beam sensitive materials in that they are difficult to run in the atom probe and challenging to image in the electron microscope. We are developing methods to enable these materials to run in the atom probe and reduce the number of images necessary for an electron tomogram to minimize electron beam damage. Additionally, we will further two 3D techniques separately and jointly – electron tomography in the scanning transmission electron microscope (STEM) and atom probe tomography (APT) – by using high resolution atomic scale imaging in 2D to complement our 3D analyses.



A 3D representation of metal nanoparticles within a mesoporous matrix. The traditional DART algorithm cannot reconstruct the particles when the number of STEM images is reduced by half (top left panel), but our new algorithm maintains the integrity and resolution.

During FY 2015, we accomplished two important goals: reduced the number of images necessary to perform a high resolution 3D reconstruction and prepared zeolites to run successfully in the atom probe. For the first goal, we combined two advanced reconstruction methods to build a new algorithm, total variation minimization (TVM), within compressed sensing (CS) and discrete tomography methods. The traditional discrete algebraic reconstruction technique (DART), which allows for 3D reconstruction with atomic resolution, could not provide accurate reconstructions when the number of images was reduced from nearly 75 images. This process deals with the algorithm used for the original solution, is a more traditional method called simultaneous iterative reconstruction technique. Our new algorithm uses an advanced method for the initial solution TVM-CS, greatly reducing the initial error and allowing 3D reconstruction of tomograms with half (or less) the initial number of images. This dramatic reduction in STEM images means that more beam sensitive materials can be probed in 3D instead of 2D. Further, the algorithm enables high resolution 3D reconstructions using energy dispersive spectroscopy or chemical imaging because each tilt angle needs to have a spectral map acquired, thus increasing beam time on the specimen.

APT is a controlled field evaporation technique that produces sub-nanoscale spatial and concurrent chemical resolutions. It works best for conducting materials because the atoms are evaporated with DC pulses. If the material is non-conductive, evaporation is thermally assisted with a laser, though obtaining controlled field evaporation can be difficult if not impossible. During FY 2015, we investigated the evaporation of zeolites in the atom probe and found that they evaporate best when coated with a metal such as chromium. Using electron microscopy, we observed that chromium deposition is not as uniform as we would like but forms "pebbles" of metal on the surface. Further, it was found that the focused ion beam preparation of needle-shaped specimens damages the crystallinity of the zeolite in a particular pattern. Steps were taken to mitigate and remove those processes that created the damage resulting in uniform evaporation of steamed and unsteamed zeolites and the 3D visualization of the change in Al distribution in the material. The Al concentration and distribution is important to understand, as they act as solid acid sites. This work was recently published in *Nature Communications*.

For FY 2016, we will expand these methods and advancements to the understanding of biological materials. Specifically, we will determine the location of heavy metal atoms within and around cells. The effect of nanoparticles in the body and brain are poorly understood and stand to be the cause or partner in cell toxicity or neurodegenerative diseases. The advancement of these techniques for understanding nanoparticle/cell interfaces will be of paramount importance.

PN15029/2704

Highly Dispersible, Thermally Stable Core/Shell Proppants for Subsurface Stimulation

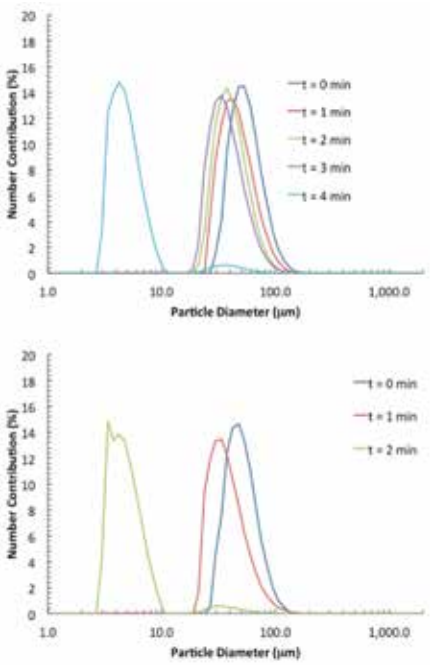
Carlos A. Fernandez

We are developing a hybrid lightweight stimulant fracturing fluid that will improve the efficiency of reservoirs and offer a more environmentally friendly technology and economically robust way to capture energy and resources.

Reservoir fracture creation and propagation by hydraulic fracturing and hydraulic shearing in enhanced geothermal systems (EGS) require the use of proppants to maintain fracture conductivity. The introduction of proppants/a stimulant with the hydraulic fracturing fluid is a common procedure in the oil and gas industry, but it has been of limited use for geothermals from the inability of common proppants to withstand high temperatures, acid fluids and treatments, and cleanouts while maintaining the porosity and permeability of the fracture. Under these conditions, proppant particles may act as nucleation sites and promote precipitation or they may dissolve, with both cases resulting in decreased fracture permeability. The objective of this project is to develop a lightweight hybrid proppant/stimulant fracturing fluid to eliminate extra steps in processing and reduce mechanical strain on pumping equipment and environmental impact. The technology from this project can potentially improve resource quality by introducing mechanical stress in the constrained subsurface environment, decreasing proppant density while optimizing proppant placement efficiency, minimizing flow back, and reducing cost.

Functionalizing sintered bauxite particles has proven to be a challenge, as the proppants have to be large enough to function as a porous agglomeration when aggregated in the fractures of the geothermal well but small enough that the polymer can reduce the density effectively and increase proppant buoyancy and settling time. Turbidity tests were performed in parallel to the recording of high-resolution videos as a function of time to learn about the stability of bare bauxite particles and polymer-functionalized bauxite particles suspensions in water. The PNNL CO_2 expanding polymers effectively functionalize the bauxite proppants surface. The settling time of the core/shell proppants in a concentration was similar to the one employed during reservoir stimulation. Samples 12 and 14 required several minutes to settle fully. The results indicate that combinations of poly(allylamine; PAA) and poly(acrylamide/sodium acrylate; PAC) are best for stabilizing the bauxite particles in solution. Using laser scattering spectrometry, this study was aided in identifying the fraction of particles that remain in solution at different time intervals and to understand the stabilizing effect of the polymer coating.

The chemical and thermal stability of best candidate proppants (Samples 12 and 14) was investigated by placing dried proppant samples in a geothermal reservoir water solution and heated inside a high pressure vessel at 250°C for 1 month to simulate the environment of geothermal reservoirs. A second set of these proppants were introduced in similar geothermal water solutions and left undisturbed at room temperature for the same timeframe to determine the baseline stability of the solutions.



Laser scattering size dispersion analysis of aqueous suspensions of core/shell (Sample 14, top) and bare proppants (bottom) as a function of settling time.

X-ray diffraction (XRD) analysis of the bare bauxite particles and polymer-coated samples showed patterns that were indistinguishable from each other. The post-stability test XRD patterns were also indistinguishable from the original materials, demonstrating high thermal and chemical stability of the inorganic cores.

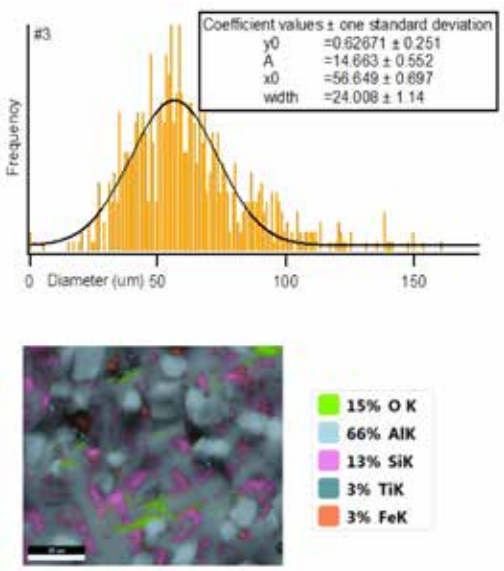
Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis examined the coating of the material and the elemental makeup of the particles. The size distribution of the samples was collected. Indication consistent with an organic polymer coating covering the inorganic bauxite particles was evidenced by the surface charging of

PN15039/2714

the particles as compared to the bare proppants. Elemental composition for both bare bauxite and polymer-coated bauxite particles was similar and corresponded primarily to aluminum and silicon with a small percentage of iron and titanium. Size distribution analysis on over 300 particles show an average size of 56 μm and a dispersion of ±24 μm, in agreement with size results obtained by laser scattering analysis on aqueous suspensions. Post-stability test SEM/EDX analysis are ongoing.

The polymer coating present on the functionalized bauxite particles was confirmed with Fourier transform infrared spectroscropy (FTIR). While the bare bauxite showed no presence of an organic coating, Sample 14 had a spectrum with the same absorption characteristics of PAC, with the coating still present after subjecting the particles to geothermal waters at 250°C for 1 month. These results provide further evidence that the polymer shell the inorganic core is stable under geothermal (thermal and chemical) conditions. The stability of the samples was also studied by mass balance analysis of the particles after the stability test at 250°C and by inductively coupled plasma optical emissions spectrometry (ICP-OES). Although firm conclusions should not be drawn from a single experiment, the mass balance of the particles was 97.6% for bare bauxite and 98.0% for Sample 14, further evidence of the high thermal and chemical stability of the core/shell proppants. Ongoing ICP/OES analysis on the geothermal waters before and after stability tests should clarify whether increased levels of Al, Si, or Fe are present in the water from dissolved bauxite particles.

Hybrid polymer/bauxite proppants were developed for use in EGS and tight oil and shale gas recovery. A variety of analytical techniques confirmed the presence of polymers on the surface of the bauxite particles and its chemical and thermal stability over an extended time frame. Functionalization of the bare bauxite particles with PAA and PAC resulted in proppants with significantly higher dispersibility in aqueous solutions as evidenced by turbidity and particle size distribution measurements. The increased stability of the core/shell proppants will eliminate the need for high viscosity carrier fluids for transporting the proppants down the borehole, reducing costs and detrimental environmental effects of currently used stimulation methods.



Top: Representative particle size distribution obtained by SEM analysis of core/shell proppants (Sample 14); Bottom: Elemental composition by EDX on core/shell proppants (Sample 14) showing primarily the presence of oxides of aluminum and silicon with small fractions of iron and titanium. Bare bauxite particles showed similar composition.

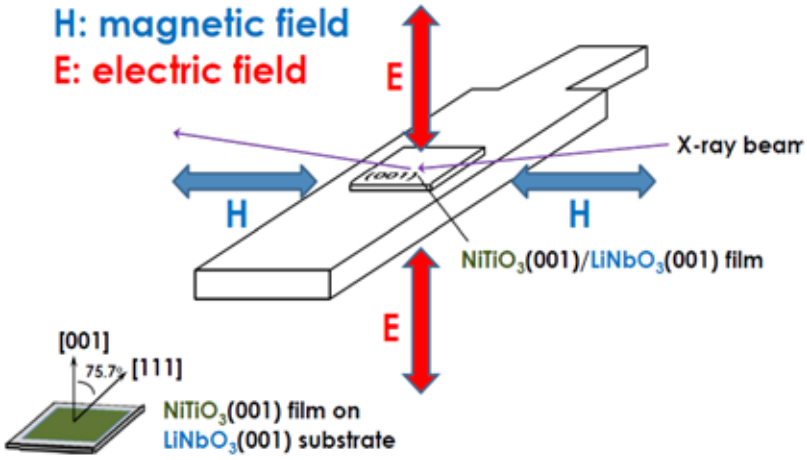
Future work will focus on the study of aggregation mechanism and investigate compression stability and conductivity of the core/shell proppants relative to traditional alternatives. A manuscript for publication is currently in preparation.

Improving Magnetoelectric Coupling in Novel Single-Phase Multiferroic Thin Films of the $MTiO_3$ (M = Fe, Mn, Ni, …) Family

Tamas Varga

The project will enable designing multiferroics via the control of chemistry and physical properties, providing key knowledge to the rational synthesis of novel materials with potential technological impacts on the information storage, energy, and semiconductor industries.

Multiferroics (materials that are both ferromagnetic [FM] and ferroelectric [FE]) can be employed as new four-state memories for future data storage applications and in photovoltaic devices for energy applications. However, the coupling of FM and FE in single-phase multiferroics is inherently weak. The objective of this work is to understand the physical origin of coupling of polarization and magnetization through theory and use that knowledge to design novel multiferroic materials that perform better. Building on our success in stabilizing $NiTiO_3$ in the theory-predicted structure in epitaxial thin film form and showing the coexistence of polarization and ferromagnetism, our hypothesis is that strain by substrate and/or via alloying/doping $MTiO_3$ will affect FM (and possibly FE) properties and, in turn, their coupling. Ultimately, we wish to demonstrate that the resulting multiferroic properties are superior to earlier results in related single-phase systems.



Experimental setup for the coupling experiment at beamline 4-ID-C of the Advanced Photon Source at Argonne National Laboratory. The magnetization vector is expected to be along the [111] direction in our (001)-grown film. A reversal of the hysteresis curves upon switching the direction of the electric field of 0.5–1.5 kV (from negative to positive) was observed in this experiment, suggesting that the electric and magnetic orders are coupled.

To control the polar and magnetic properties by strain, we synthesized multiferroic $NiTiO_3$ on sapphire Al_2O_3 substrates by epitaxial growth using pulsed laser deposition (PLD). Epitaxial $Ni_{1-x}Ti_{1-y}O_3$ films of different Ni/Ti ratios and thicknesses were deposited on Al_2O_3(001) substrates by PLD at different temperatures and characterized using several techniques. The effect of film thickness, deposition temperature, and film stoichiometry on lattice strain, film structure, and physical properties was investigated. We argue that the more Ni is in the structure, the stronger antiferromagnetic (AFM) ordering becomes. Therefore, the AFM ordering temperature becomes higher as the thermal energy needed to destroy the ordering becomes larger. We found that the desired phase (*R3c*) of $NiTiO_3$ was stabilized in films of up to at least 30 nm thickness. From $NiTiO_3/Al_2O_3$ films and the conditions examined in our study, a 20–30 nm film with up to 30% excess Ni would be the most promising multiferroic material. Our ability to control the magnetic properties by strain engineering suggests that pushing the Néel transition closer to room temperature in $MTiO_3$ phases may be possible, especially if one considers doped structures as well in future work.

Next, we explored the effect of substrate-exerted strain on the films grown on three different substrates, each representing a different strain state. We investigated the dependence of the polar and magnetic properties on strain. Epitaxial $NiTiO_3$ films were deposited on Al_2O_3, Fe_2O_3, and $LiNbO_3$ substrates by pulsed laser deposition, and characterized using several techniques. The effect of substrate choice on lattice strain, film structure, and physical properties was investigated. Our structural data from X-ray diffraction and electron microscopy showed that the choice of substrate had a marked effect on the structure and crystalline quality of the films. Physical property measurements reveal a dependence

PN13072/2553

of the induced FM on the substrate-exerted strain as we compared films grown on sapphire Al_2O_3 (large compressive strain), hematite Fe_2O_3 (close match, no strain), and $LiNbO_3$ (tensile strain) substrates. As strain increases, the residual magnetization (FM) in the films increases.

We explored the polar properties of the $NiTiO_3$ films using optical second harmonic generation (SHG), which occurs only in the absence of inversion symmetry, a necessary condition for a polar medium such as a ferroelectric. It should not occur for a non-polar substance such as the sapphire substrate or non-multiferroic, ilmenite-type $NiTiO_3$. Having demonstrated that the non-polar sapphire substrate shows no signal; therefore, any observed SHG contrast comes from the film. We thus performed optical SHG on a three $NiTiO_3$ samples: Al_2O_3, Fe_2O_3, and $LiNbO_3$. Qualitatively comparing the three images, we found a correlation between strain and polarization: the Fe_2O_3 sample shows essentially no SHG signal, while the Al_2O_3 sample exhibits significant SHG, indicating that the film is polar. The strong SHG response of the $LiNbO_3$ sample should be dominated by the ferroelectric substrate; therefore, it is not indicative of the substrate strain. Nevertheless, comparison of the Al_2O_3 and Fe_2O_3 samples supports the assumption that polarization in our $NiTiO_3$ films is strain-induced. These findings highlight our ability to control the ferroic properties in $NiTiO_3$ thin films by the choice of substrate. From the substrates studied here, the perovskite substrate $LiNbO_3$ proved to be the most promising one for strong multiferroism. Our results are consistent with the theory prediction that ferromagnetism in acentric $NiTiO_3$ is polarization-induced.

We sought to improve the crystalline quality for the metastable *R3c* structure in $NiTiO_3$ by post-synthesis annealing of $NiTiO_3/Al_2O_3$ films at different temperatures in air. From the characterization of samples annealed at 300, 600, and 1000°C temperatures (4–8 hr periods), annealing at 600°C was found to improve the structural as well magnetic and polar properties. Only in samples annealed at 600°C did the desired *R3c* phase persist. Higher annealing temperature (1000°C) resulted in ordered R3-type $NiTiO_3$ as major phase (before phase segregation that happens after longer annealing times).

The most intriguing result of FY 2015 was the first-time demonstration of the 2008 theory that predicted multiferroic behavior in $MTiO_3$ compounds (M= Fe, Mn, Ni) crystallizing in the $LiNbO_3$-type structure. In a synchrotron experiment targeted at demonstrating the coupling between ferroelectric polarization and ferromagnetism in $NiTiO_3/LiNbO_3$ films, we utilized the unique interaction of the left- and right-polarized X-ray photons with the magnetic domains of the sample oriented in field. XMCD spectra and magnetic hysteresis curves were collected under magnetic field at low temperature (sample cooled below 80 K, under the Néel transition temperature), and under electric field of up to 200 kV/m to pole the sample. The film is ferroelectric, therefore it was polarizable. The cooled sample with the applied magnetic field exhibit ferromagnetic domains all oriented in the direction of the field. Next, we established an imbalance in the magnetic domain populations produced by application of the electric field in a certain direction. After switching direction of the electric field by 180 degrees, the reversal in the orientation of the magnetic domains was observed, manifested in a change in the magnetic hysteresis curves.

Finally, we started ferroic domain structure simulations using mesoscale-based phase-field modeling with the goal of learning how domain structures are affected by strain and synthesis conditions in $NiTiO_3$ films. Our preliminary modeling results suggested a patterned domain structure in our material when the magnetization (M) vector is along [111] or [-1-1-1] direction, while a single domain was predicted when the magnetization vector is perpendicular to the predicted direction.

PN13072/2553

Improving the Performance of Li-Air and Li-S Batteries Using Polymeric and Metallic Nanomaterials

Priyanka Bhattacharya

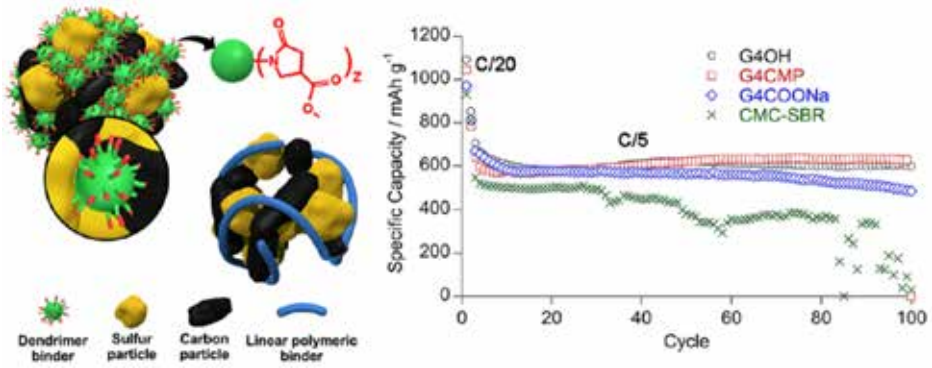
This project developed novel nanomaterials to enhance the performance of lithium (Li) batteries and understand their fading mechanisms.

An increased demand for high energy density batteries based on environmentally friendly materials has led to the research and development of rechargeable Li batteries, which include Li-air (Li-O_2) and Li-sulfur (Li-S). A challenge with the Li-O_2 battery is recharging the insoluble, poorly conducting Li_2O_2 discharge products to Li^+ and O_2 during charging. Hence, Li-O_2 batteries require electrocatalysts for reducing the over-potentials of the oxygen evolution reaction. For Li-S batteries, charge/discharge involves the creation of highly soluble polysulfide intermediates in electrolytes, causing an irreversible loss of active sulfur. Our efforts are directed toward polymers and nanostructures to trap polysulfides, thus improving the electrochemical cell cycling. The remarkable physico-chemical properties of dendrimers motivated research into the application of dendrimer-encapsulated Ru electrocatalysts in Li-O_2 batteries and their application in trapping polysulfides in Li-S batteries. Thus, our objective is to identify novel, efficient materials for high energy density applications and place PNNL at the frontier of dendrimer research in energy storage.

Dendrimer-encapsulated ruthenium nanoparticles (DENs) as catalysts in Li-O_2 batteries. In FY 2013, we synthesized monodispersed and stable DEN of average size (~2 nm). Once complexation between the dendrimers and Ru^{3+} was complete, the Ru^{3+} were chemically reduced *in situ* to Ru metal using 10 molar excess of $NaBH_4$. Complexation and reduction were monitored using UV-vis absorption spectroscopy. After reduction, DEN solutions were dialyzed using 10,000 MWCO dialysis membranes to remove impurities. The average size of the DENs with both the hydroxyl and amine terminated dendrimers was ~2 nm. However, while the hydroxyl-terminated DEN solutions remained stable for over 2 months, amine-terminated DENs aggregated within a few days because some of the Ru^{3+} complexed with the primary amines of the dendrimers that when reduced remained at the periphery of the dendrimers and unprotected, leading to aggregation over time. Subsequently, all experiments were conducted using hydroxyl-terminated DENs (G4-OH).

PAMAM dendrimers encapsulating nanoparticles demonstrated the potential for being catalysts in Li-O_2 cells. The DENs were stable for months and electrochemically stable toward Li metal and electrolyte solvents. The materials improved the cycling efficiency of KB carbon by nearly 3.3 times and lowered the charging over-potential by almost 0.4 V, creating a new state-of-the-art catalyst for Li-O_2 batteries. Most importantly, the amount of Ru used as a catalyst is 10 times less than that in current state-of-the-art published work. Thus, dendrimer-stabilized Ru nanoparticles enable use of a much lower amount of the noble metal catalyst.

To analyze the nature of discharge products, scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy were conducted on discharged cathodes that were washed in dimethoxyethane (DME) for 3 days to remove electrolyte salts. Both SEM and XRD showed the presence of Li_2O_2 as the major discharge product, with some electrolyte decomposition products also observed. Charged cells showed little or no Li_2O_2, suggesting good rechargeability. XRD and XPS results showed the presence of ruthenium oxide (RuO_2) rather than Ru metal, with oxygen adsorption on Ru metal surface in ambient conditions. This scenario indicates that O_2 diffuses into the dendrimer periphery and enables the use of



Left: Schematic of dendrimer binder and linear polymeric binder interactions with carbon/sulfur composite; Right: Electrochemical cycling data of Li-S cells with dendrimer binders and CMC-SBR binder.

PN13013/2494

RuO_2, recently shown to be better OER catalysts than Ru metal. Results from this work were presented at three international conferences, and a paper was published in *Advanced Functional Materials*.

With an aim to synthesize metallic Ru nanoparticles encapsulated within dendrimers, we employed ethylene glycol as the solvent medium in FY 2015. We discovered that while the DEN-Ru formed were again rapidly oxidized when exposed to air, their size was reduced (average size ~0.7 nm). Thus, the same dendrimers with similar amounts of precursor Ru^{3+} (~20:1 = Ru^{3+}:dendrimer) in aqueous solutions resulted in nanometer-sized particles, where in ethylene glycol solvents, subnanometer-sized particles were formed. Generation 4 PAMAM dendrimers with 4-carbomethoxypyrrolidone surface groups were used in this study. To understand the coordination mechanisms in the two solvents, XPS and NMR experiments were conducted. Interesting insights were obtained from both experiments: first, XPS results indicated that while in the ethylene glycol solvents, Ru^{3+} coordinated majorly with dendrimer surface groups in aqueous solutions, with the coordination occurring with the interior functional groups. Next, NMR results were contradictory to XPS results, where a more compact structure of dendrimers was observed in ethylene glycol. However, the coordination of Ru^{3+} was similar (i.e., within the dendrimers in both solvents). While XPS samples were prepared by drop-casting and drying the solutions on silica substrates, the NMR experiments were conducted on liquid samples. This intriguing disparity in the observations from the two different experimental techniques reveal important information about the global structure of the dendrimers in the two different solvents in solid and liquid state, suggesting backfolding of their surface groups in solutions. The DEN-Ru synthesized in ethylene glycol also showed three times better catalytic activity towards hydrogen evolution reaction with ~3000 s^{-1} turnover rates. As of FY 2015 end, a manuscript on this work is being prepared.

Dendrimers for capturing polysulfides in Li-S cells. In FY 2014, we developed novel electronically conducting dendrimers. PAMAM dendrimers are inherently non-conducting. To employ them as cathode materials in Li-S batteries, we synthesized electronically conducting PAMAM dendrimers by modifying their surface groups with poly(3,4-ethylenedioxythiophene; PEDOT). Hyperbranched polymers were also modified for a commercially viable approach. Dendrimer-based PEDOTs were more conducting than hyperbranched based systems. We were able to improve the conductivities using lower generation dendrimers and achieved conductivities as high as 1 S/cm. These modified dendritic polymers were used to make sulfur composite cathodes and their performance tested in Li-S cells. Initial results indicated good cycling stability and electrochemical stability of these modified polymers in the Li-S cells. Preliminary results were presented at three international conferences, and at the end of FY 2015, a manuscript is in preparation in collaboration with our industrial partners Dendritech, Inc. and Nanosynthons, LLC.

Toward the end of FY 2014, we began investigating the applications of dendrimers as functional binders for high loading S cathodes. PAMAM dendrimers with several different surface functional groups were explored, out of which hydroxyl and 4-carbomethoxypyrrolidone terminated PAMAM dendrimers showed the best performance. The electrode materials slurry was prepared by rigorously mixing 10 wt% dendrimers with 80 wt% Super-P-S composite and 10 wt% multi-walled carbon nanotubes conductive carbon additive in aqueous solutions. Cathodes were prepared by coating carbon-coated aluminum foils as current collectors with the slurry. The water was dried out at 60°C under vacuum overnight, and electrodes were punched out. Li-S coin cell testing was done at 0.05 C and 0.2 C rates (1 C = 1673 mAh g^{-1}). We have successfully fabricated pinhole and crack free high loading S electrode coatings (~4 mg cm^{-2} sulfur) using "standard" (not specifically tailored) materials and simple processing methods. An exceptional electrochemical cycling performance was obtained (compared to cathodes with conventional linear polymeric binders such as carboxymethyl cellulose [CMC] and styrene-butadiene rubber [SBR]) with >100 cycles and 85–98% capacity retention, which was attributed to better interfacial interactions between the high density of surface functional groups of the dendrimers and the C/S composite materials as well as better electrolyte wetting due to the dendrimer nanoscale spherical molecular, porous architectures. The dendrimer-based binders also physically and chemically trapped the polar polysulfides, enhancing the cell cycling stability and demonstrating the significant utility of this new binder architecture that exhibits critical physicochemical properties and flexible nanoscale design parameters (CNDPs) potentially applicable to electrochemical systems beyond Li-S batteries. A manuscript based on this work is currently under review with *Nano Energy*.

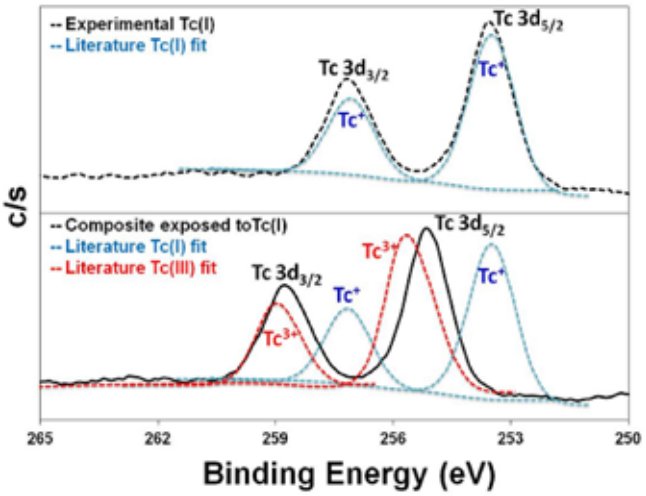
In this project, we successfully demonstrated novel materials based on dendritic macromolecules with remarkable physicochemical properties that can be used in high-energy density lithium batteries and in other energy storage and conversion devices. This research has generated five manuscripts (published, in review, and/or submitted) to date, and the results have been presented at 12 international and local meetings. Future work will focus on developing commercially viable hyperbranched materials for the above applications by incorporating the specific functional properties of their structurally perfect counterparts, dendrimers.

Inorganic Composites for Tc Alternative Waste Forms

Tatiana Levitskaia

This project investigates new technologies for the separation of technetium-99 (Tc) from low-activity waste (LAW) and the immobilization in non-glass alternative waste forms.

The long half-life, complex chemical behavior in tank waste, limited incorporation in mid- to high-temperature immobilization processes, and high mobility of some species in subsurface environments make Tc one of the most problematic long-lived contaminants at the U.S. DOE Hanford Site. In strong alkaline environments typical of Hanford tank waste, Tc exists predominantly in liquid fractions as oxidized Tc(VII) in the chemical form of TcO_4^- (pertechnetate). Reducing conditions, high radiation fields, and the presence of organics and noble metal catalysts promote Tc formation in lower oxidation states, collectively known as non-pertechnetate species. Previous reports indicate that these species are consistent with derivatives of Tc(I) carbonyl complexes such as $[Tc(CO)_3]^+$ or $[Tc(NO)(CO)_2]^{2+}$.



XPS spectra of the $[Tc(CO)_3]^+$ non-pertechnetate species before and after incorporation into the Bi(III)-Co(II)-Al(III) composite matrix.

While pertechnetate can be removed from the tank, no methods currently exist for either the direct separation of non-pertechnetate species or control of their redox behavior for immobilization and long-term storage. These uncertainties affect development of overall Tc management strategies during Hanford tank waste processing. This project is developing inorganic materials for the selective separation and immobilization of total Tc in non-glass waste forms. Preliminary results indicate that layered inorganic composite materials similar in structure to anionic clays are promising, and the composition of these materials can be tailored to control Tc redox behavior to achieve selective uptake of TcO_4^- and/or non-pertechnetate species and enhance their interaction with the solid matrix.

A library of inorganic composite materials was developed and tested for the uptake species TcO_4^- and $[Tc(CO)_3]^+$. These materials typically consist of 2D nano-structured divalent cations octahedrally coordinated by hydroxide ions, where some of the divalent cations are isomorphously replaced by tri- or tetravalent cations. Such a replacement results in charged intercalated with interchangeable hydrated anions. Control of the Tc oxidation state is achieved by introducing redox active centers in the composite structure to maintain Tc in the desired oxidation state and to suppress its oxidation to Tc(VII) upon exposure to the alkaline environments such as those typical for cements and release as TcO_4^- anion. These redox active centers convert the mobile Tc(VII) or Tc(I) species to the significantly less mobile oxidation states such as Tc(IV) through redox reaction, suppressing the reverse reaction and enhancing Tc immobilization within the composite matrix.

The choice of the appropriate redox metal center incorporated into the composite structure is guided by our previous electrochemical studies performed using aqueous solutions containing high sodium nitrate and variable sodium hydroxide concentrations typifying the Hanford tank waste supernatants. The maximum potential required for TcO_4^- reduction to Tc(IV) and formation of TcO_2 was measured to be +0.55 V, and such reductants as tin (Sn) possessing standard redox potential of 0.93V ($E^0_{Sn(IV)/Sn(IV)}$=0.93V) can reduce Tc(VII) to Tc(IV). Indeed, several previous reports have demonstrated this reduction process to occur using $SnCl_2$ or related compounds. However, the mechanism of Tc uptake into the matrix of Sn(II)-containing solid materials has not yet been elucidated.

We demonstrated that Sn(II) composites exhibit efficient TcO_4^- uptake capacity (95–98%), and mechanism of TcO_4^- uptake was elucidated using representative Sn(II)-Al(III)-phosphate material. X-ray powder diffraction (XRD) results demonstrated

PN15040/2715

reduction of TcO_4^- to TcO_2 accompanied by the oxidation of SnO to SnO_2. This result is in agreement with the analysis of this material using X-ray photoelectron spectroscopy (XPS), which confirmed Tc(VII) reduction to Tc(IV) upon uptake by Sn(II)-Al(III)-phosphate composite. Transmission electron microscopy (TEM) images of the Sn(II)-Al(III)-phosphate composite show bundles of crystalline fibers embedded within amorphous matrix. The fibers are low in aluminum and rich in tin; however, the matrix has high aluminum and low tin content. Interestingly, both amorphous matrix and crystalline fibers uptake Tc. However, Tc is significantly concentrated by the crystalline fiber bundles, suggesting high affinity of TcO_4^- toward Sn(II).

Sn(II)-Al(III)-phosphate composite was tested for uptake of TcO_4^- from 7.8M Na^+ LAW simulant solution with and without chromate, which commonly interferes with TcO_4^- uptake by Sn(II) materials due to the similar Tc(VII)/Tc(IV) and Cr(VI)/Cr(III) reduction potentials in the alkaline solutions. Sn(II)-Al(III)-phosphate composite demonstrated fast and highly efficient Tc(VII) uptake from the LAW simulant with the equilibrium K_d values approaching 10,000. Even though the presence of Cr(VI) reduced $K_d(TcO_4^-)$ values, the uptake efficiency remains sufficiently high for the practical removal of TcO_4^- from LAW. The kinetics of the uptake was not affected by the presence of chromate.

It was found that non-pertechnetate $[Tc(CO)_3]^+$ species can be effectively removed from solutions containing high nitrate concentration by Bi(III)-based composite materials. The XRD analysis showed that prepared Bi(III)-Co(II)-Al(III) material contains two crystalline phases. One phase has layered hydrotalcite-like structure presumably consisting of Co(II)-Al(III) framework. The second phase is consistent with the structure of bismutite $Bi_2(CO_3)O_2$, which also has a layered arrangement. Incorporation of Tc(I) does not produce prominent phase changes potentially suggesting the incorporation of Tc(I) in this layered structure of the composite. The oxidation state of non-pertechnetate species was assessed by the XPS measurements. The prepared $[Tc(CO)_3]$+ complex exhibits characteristic Tc(I) photoemission. When it is incorporated in the Bi(III)-Co(II)-Al(III) composite structure, the photoemission energy of the absorbed Tc species appears between the energies of the reference Tc(I) and Tc(III) species suggesting that Tc(I) is oxidized to Tc(II). To our knowledge it is the first XPS observation of the Tc(II) species.

Overall, the performed investigation significantly contributed to the understanding of the Tc redox chemistry and of the mechanism of Tc uptake and incorporation into the inorganic solid composite matrices.

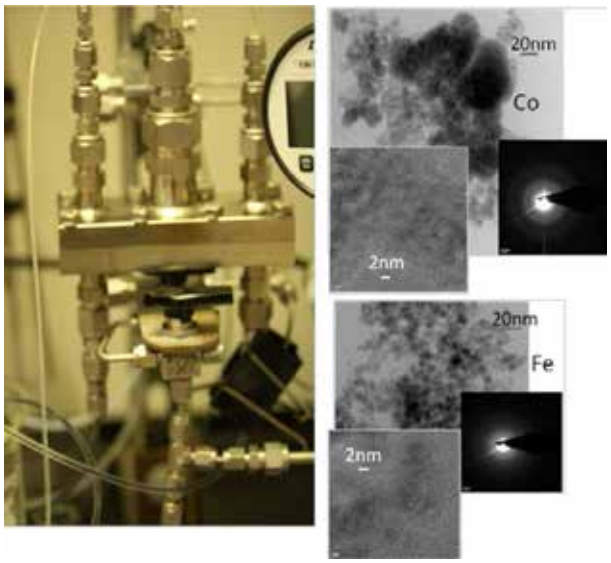
Membrane Reactor-Enabled Manufacturing Processes of Nano-Metal Particles

Wei Liu

We are developing membrane reactor concepts as one scalable, new material processing technology for the synthesis of transition metal nano-particles (Fe, Ni, Co) at low cost.

The nano-sized transition metals have the potential for widespread uses as specialty bulk materials, functional materials such as soft magnets, and advanced catalysis. Compared to a great number of publications on nano-particles of noble or precious metals (Pt, Pd, Au, Ag), studies about the transitional metal particle are limited. One hindrance is lack of low-cost, scalable manufacturing methods to produce sufficient quantities of nano-transition metals for new product and/or process prototype development. For this project, a membrane reactor process is proposed as the first-of-its kind synthesis of nano-transitional metal particles through liquid-phase reactions. The reactor comprises two sets of micro-channels separated by a porous membrane for the feed and sweep flow. The feed fluid containing metal precursors such as a metal chloride solution is injected into the sweep fluid that contains a reducing agent as nano-droplets via the membrane pore. The metal ion in the droplet is reduced into nano-metallic particles inside of the membrane channel.

The membrane reactor is a scalable, efficient way to divide a bulk fluid into uniform nano-sized droplets. Each membrane pore functions as a nano "inkjet" nozzle, with the droplet size controlled by the pore opening. For a membrane sheet comprising 50 nm pores at 10% surface porosity, it is equivalent to ~ 5 billion nano-ink jets per 1 cm^2. The membrane reactor also has a nearly linear scale-up rule. After the fundamental concepts are demonstrated and material properties understood, production can be enlarged by increasing the membrane area. Dispersion and reaction in the membrane reactor is a continuous process, with mixing and reaction intensified in the micro-flow channels. Thus, high productivity of the membrane reactor will lower the manufacturing cost.



Left: The membrane test cell built and used in this work; Right: Transmission electron microscopy (TEM) pictures of the nano-Co and Fe particles. Bottom: Brunauer-Emmett-Teller (BET) surface area and magnetic property measurements of two groups of samples.

Sample	BET surface area m^2/g	nm	Sample	Magnetic property M (emu/g)	Hc (Oe)
Fe #1	134.0	5.7	Fe	111.0	442.0
Fe #2	153.0	5.0	CoFe	62.3	442.0
Co	62.1	10.9	Co	55.2	64.0

BET surface area and magnetic property measurements of two groups of samples.

In FY 2015, we identified an optimum membrane by screening commercial and in-house membranes, conducted parametric tests of nano-particle production with different feed concentrations and flow rates, and measured properties of resulting nano-particles with TEM, BET, X-ray powder diffraction, and scanning electron microscope surface area. The major learning and results are summarized as follows:

- Conversion of transition metal ions into metallic particles (Co, Fe, and Ni) can be completed in the reactor at a very short residence time at room temperature.
- Nano particles could not be formed if the membrane is broken or leaks.
- Nano-particle productivity as high as 5 kg/m^2/h was demonstrated.
- The nano-particle size is within the range of 2 to 11 nm.
- The resulting nano particles show the state-of-the-art BET surface area and magnetization strength.

A promising, scalable process was demonstrated for the production of nano-metal particles at high throughput and competitive costs. The resulting nano-metal particles were so active that they were readily oxidized when exposed to ambient air or water. The protective and stabilization methods need to be improved, however, as it was found that impurities in the reacted solution mixture can be substantially removed by proper washing. It is expected that the magnetic strength can be enhanced by removing those impurities. The correlation of reaction conditions with the particle size and properties are recommended for future studies.

PN14017/2601

Meso-Scale Science and Technology: Manufacturing of Nanostructured Soft Magnetic Materials

Jun Cui

We are developing novel consolidation methods to enable robust, economical manufacturing of nano-structured bulk soft magnetic materials to benefit the United States in both energy security and technology leadership.

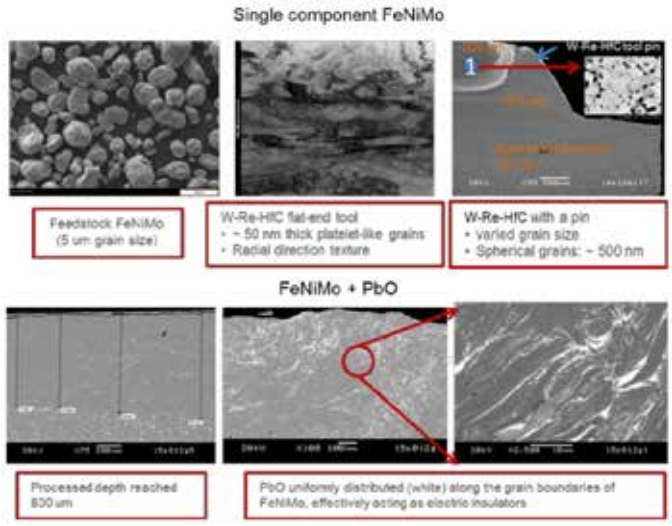
Soft magnetic materials are integral components of motor and power electronics that process over 80% of the world's electricity. The global market of soft magnetic materials reached $45 billion in 2014 and is estimated to be $67 billion in 2019. However, current soft magnets have two major limitations: energy loss and overheating. Soft magnetic components result in 9% loss during electricity transmission and distribution, accounting for both $25.8 billion in lost revenue and additional CO_2 emissions. In addition, efficiency and size advantages afforded by power electronics incorporating wide bandgap semiconductors cannot be realized due to overheating of soft magnet components.

The aforementioned limitations arise from the intrinsic eddy current and hysteresis losses in soft magnetic materials. Advanced soft magnetic materials (ASMMs) with a tunable combination of magnetization, coercivity, permeability, and electrical resistivity can potentially result in higher efficiency, smaller size, and lower cost for power conversion devices. With today's limited manufacturing methods, ASMMs are available only in laminated forms such as sheet steels or Fe-Co-based nanocrystalline/amorphous thin ribbon (~20 µm thick) and cannot be used widely due to either higher processing cost or unfavorable mechanical robustness. As a result, economically manufacturing nanostructured bulk soft magnetic materials with lower coercivity (lower hysteresis loss) and/or increased electrical resistivity (reducing the eddy current loss) is top-of-the-line in soft magnets.

The objective of this project is to understand the thermodynamic and kinetic laws that govern formation of nanostructures in bulk materials and develop cost-effective methods to produce nanostructured bulk materials. Enhanced shear consolidation and spark plasma sintering, being non-equilibrium processing systems exploiting a unique combination of thermodynamic and kinetic parameters, are identified as the promising methods to attain nanostructured bulk materials. We have thus focused on developing an enhanced shear consolidation method and collaborating with external resources on spark plasma sintering.

In FY 2013 and FY 2014, a meso-scale phase field model was developed to investigate the mechanisms of nanocrystalline structure formation and evolution in a Cu-doped FeSi system. The role of Cu in the grain refinement of FeSi was found to result in both nucleation and grain boundary pinning. In addition, an enhanced shear consolidation was modeled using 3D smoothed-particle hydrodynamics (SPH) able to predict the temperature trend profile as a function of load, plunge rotation speed, and process duration. Combined with a better understanding of feedstock materials and temperature control system, the SPH model could be used to predict the temperature profile accurately and help guide experimental designs.

FeNiMo flakes (~1 × 50 × 50 µm^3, ball milled melt-spun ribbons) and FeNiMo gas atomized powders (~5 µm grain size) were successfully consolidated into fully dense pucks (3 mm thick, 25 mm diameter) with sub-micron microstructure (~500 nm). Consolidated FeNiMo from flakes showed signs of decomposition suggested by the $FeNi_3$ precipitates observed, indicating the processing temperature exceeded the maxi-



Microstructures obtained from SEM and TEM

PN13061/2542

mum allowable temperature. The consolidated FeNiMo from powders has seen platelet-like structure with a grain scale of 50 nm along the load direction. The extent of grain refinement (5 µm to 50 nm) is an achievement for solid-state processing technologies that will have an immediate profound impact on the engineering community. In addition, electrical resistance was improved by nearly 50%, while magnetic properties were left unchanged.

We continued our efforts on consolidating FeNiMo using different tool materials, different profiles, and different times of processing at one setting. In addition, we incorporated PbO as an electrical-insulating material into the FeNiMo system with the goal of increasing electrical resistivity of the FeNiMo soft magnet. The results are shown, with a selective summary of the microstructures and functional properties of the consolidated FeNiMo.

Tool profiles and processing parameters, including load and cooling regimes, play a significant role on the microstructure obtained. For instance, in the single component FeNiMo, we found that consolidation using a W-Re-HfC flat-end tool resulted in a radial direction texture with platelet-like grains, where the W-Fe-HfC tool with a pin led to a microstructure with a varied grain size depending on the distance from the tool and spherical grains were obtained. In the composite of FeNiMo with 10 wt% PbO, a relatively uniform distribution of the PbO was observed along the grain boundaries. It should be noted that further optimization is needed for the grain scale of the FeNiMo component.

Comparing the functional properties of the consolidated FeNiMo, the magnetization—intrinsic magnetic properties— was not affected by the processing tools and conditions. However, there was a large variation on the coercivity, which was expected due to the different microstructures. The optimal electrical resistivity was twice that of the commercially available counterpart. The incorporation of PbO did not increase the electrical resistivity as intended probably due to the lack of homogeneity of the microstructure. In addition, the optimal weight fraction of the PbO is in need of further investigation, and the effect of microstructure on energy core loss also requires additional research and understanding.

Overall, we made progress in FY 2015 in developing the capability of manufacturing FeNiMo soft magnets using solid-state processing. It is understood that in enhanced shear consolidation, processing tool, load, torque, and cooling/heating regime all affect the resultant microstructure, hence the properties. The complexity of this technique involving independently tuning the processing parameters necessitates more trial runs in this specific materials system. The structure-property relationships obtained to date provide future direction for using enhanced shear consolidation to develop soft magnetic core materials with better performance.

Modeling the Interfacial Effects, Partitioning, and Production Routes of Epsilon Particles in Uranium Oxide

Jon Schwantes

The goal of this work is to elucidate physical and chemical mechanisms that govern the formation of metallic inclusions in irradiated fuel to understand the radiological, physical, and chemical conditions leading to their formation and unique properties.

The chemical fractionation of five-metal "epsilon phases" from nuclear fuel under irradiation is not well understood. The development of these phases within uranium oxide matrices over time in fuel under irradiation has been linked to many important phenomena over the life cycle of nuclear fuel, from in-reactor operations to long-term spent fuel disposition. It has been hypothesized that epsilon phase formation can affect fuel performance, control cladding erosion, and cause stress corrosion through both the physical disruption of the fuel matrix caused by growth and the alteration of the fuel's electrochemical behavior caused by presence as a unique chemical species.

This effort aims to understand the formation mechanisms of the epsilon metal phase during nuclear fuel irradiation and to understand the solid-solid-gas interfacial equilibrium effects that lead to variations in the properties of this unique phase. Developing a fundamental understanding of the chemical, radiological, and material structure conditions that led to precipitation of these phases will significantly improve our knowledge of nuclear fuel under irradiation conditions.

The expected outcomes of this research project are to characterize the epsilon metal phase and reveal the driving factors that produce epsilon metal precipitates in uranium oxide (UO_2). Some of the challenges we will tackle and queries we intend to resolve include the following:

- Are epsilon metals in used nuclear fuel a single phase or a mixture of several phases?
- Are these phases composed of fission product elements, activation product elements, or a mixture of both?
- At what concentration or key burn-up levels do we expect to see epsilon phases form as precipitates?
- Is zirconium from cladding or other fission products required to precipitate epsilon metals?
- Are the unique effects of the radiation environment required for epsilon phase precipitation at reactor conditions?
- What (if any) deleterious effects do epsilon metals have on the thermal and mechanical behavior of UO_2 during and after irradiation?
- What is the solubility of various metals in UO_2, and why are these metals more soluble in UO_2 when produced *ex situ* of a reactor (observation approached 10 wt% or 100,000 ppm) compared with the concentration of precipitated epsilon metals (1 wt% or 10,000 ppm)?
- What is the effect of epsilon metal incorporation on the irradiation behavior of nuclear fuel? Is the final precipitate/solid solution ratio of metals in epsilon phase stable or evolving during burn-up?

A very late FY 2015 start, this project had only a few accomplishments planned or achieved. Many of the milestones are tied to instrument and software license purchases, including scanning transmission electron microscope detector for the Radiochemical Processing Laboratory's dual beam focused ion beam/scanning electron microscope and both a VASP and MICRESS version 6.0 license. Other less tangible accomplishments include using this project (and others) to support staff conversion and helping several new postdoctoral fellows.

Technical work during FY 2015 was focused on setting up the modeling frameworks that this project will use over its lifespan. Competing physical mechanisms for epsilon phase formation have been developed based on dominant compositions of fission or activation product elements, and schemes for evaluating these mechanisms using density functional theory (DFT) have been created. For fission product elements, mobility of individual elements to grain interstices during irradiation is expected, and calculations of the energetics of element impurities on the bulk UO_2 lattice are anticipated to provide information about the relative driving force associated with this mobility. For a primarily activation element composition, reactive gas transport of MoO_x and RuO_4 is expected to be the primary formation mechanism, and DFT calculations are planned to evaluate the reduction, deposition, and epsilon phase formation mechanisms.

PN15100/2775

Nanocomposite Particle Synthesis Using Switchable Ionic Liquids

David J. Heldebrant

We are developing a new methodology for synthesizing magnetic FeCo nanocomposites using switchable ionic liquids with the benefits of controlled morphology and reduced waste, synthesis rate, and scalability.

This project is about understanding the processes of controlled homogeneous nucleation and the growth of nanocomposite materials in supersaturated solutions. We are identifying key scientific principles to enable the predicable scalable synthesis of nanomaterials in kg quantities by studying the nucleation of FeCo nanocomposite nanoparticles in switchable ionic liquids (SWILS). The polar ions of the SWIL can be used to solvate individual metal atoms at high concentrations, creating a "soft template" sphere of ions in a heterogeneous liquid solution. These features may offer unprecedented finite control of solvation, leading to controlled nucleation and the separation of mono-disperse particles. The results will provide scientific principles critical for understanding controlled nucleation without growth, putting PNNL at the forefront of the inscalable solution synthesis of nanocomposite particles with precise control over particle size, shape, and morphology. To this end, six hypotheses were tested during FY 2015 as described in detail below.

Establish super-saturation of metal precursors. We previously attempted to optimize pairing metal atoms (Fe and Co) with chelates of preferred hardness or softness, which we tested with SWIL systems. Different trigger gases matched the texture profiles of the metals, and Fe preferred alkylcarbonates to xanthates, suggesting that CO_2 would be the gas of choice for subsequent experiments.

Characterize solvation sphere with ToF-SIMS, NMR, and IR. Offline NMR and IR characterization of the primary solvation sphere was inconclusive from the paramagnetism of iron precursors and strong carbonate absorption bands. To maximize our SWIL approach, we must understand the formation of soft template structures and their compositional changes as a function of varying solution conditions. We had proposed to study multiple templates with different coordinating anions prepared by changing the acid trigger gas. We attempted to identify the primary or secondary solvation sphere of the metal atoms. Initial spectroscopic characterization of species was be studied by spectroscopic methods such as *in operando* NMR and IR, though neither proved useful due to paramagnetism and detector saturation, respectively, as these two spectroscopy methods have yet to be successful in characterizing the solvation environment.

Promote nanoparticle formation. We observed microdroplets of ionic domains with dissolved metal salts in the methanol, which confirmed the existence of soft-template ions. While our methods have yet to recreate this phenomena in the neat liquid, we hypothesize that these microdroplets are key to forming solution particles. Performed with another program, dynamic simulations of SWIL molecules showed the ionic domains of liquid on the order of 2–5 nm, the size of Fe_2O_3 particles produced from SWIL experiments. Also, SEM and TEM imaging has shown that these droplets aggregate over time and can grow anisotropic materials. These observations suggest that the microdroplets are in fact acting as the soft template for nanomaterial growth.

Cap particles with SWILs. Via microscopy, we observed organic electrolyte coatings on produced particles, indicating that an ionic (soft template) coating remains, capping the particles and enabling safe handling to deliver to other groups for consolidation.

Understand reversible water sorption/expulsion behavior of rods. We synthesized carbon/Fe_XS_Y(C) rods with 20–100 nm thickness and 1–10 µm length using SWIL made from a mixture of 1,8-diazabicycloundec-7-ene (DBU), 1-hexanol, a trigger component (CS_2), and $FeCl_3$ as catalyst at 180°C. Fe-coordination and electrosteric environment favors the self-catalytic growth of rods. At 180°C, the synthesized material appeared as high aspect ratio bundles composed of individual smooth fibers on the order of tens of nm wide. When carbonized at 600°C for 6 h under nitrogen, individual smaller fibers appeared to coalesce into cross-linked larger single bundles that had a sharp, bright striation on the long axis. The effect of temperature solvent (DBU and hexanol) has been investigated, and heating SWIL-CS_2-$FeCl_3$ solutions to 170–180°C was necessary for nanorod formation.

Understand reversible water sorption/expulsion behavior via chemically induced phase changes inside the rods. To understand the effect of water on carbon/Fe_XS_Y(C) nanorods,

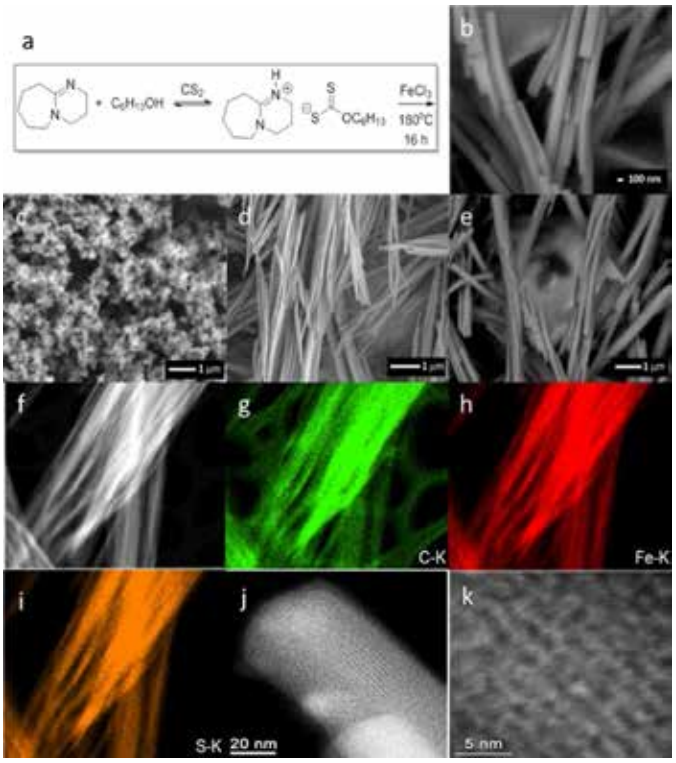
PN14057/2641

adsorption behavior of water was studied. We envisioned that the presence of heteroatoms (oxygen and sulfur) on carbon would favor high water adsorption mainly governed by functionalities that form hydrogen bonding with water. When the RH reached 50–80%, the weight of the material decreased rapidly, possibly due to re-organization of functional groups or structural phase changes. This unprecedented water or other gas expulsion behavior at high RH is not known in inorganic materials, including zeolites, carbon, and MOFs.

We took a closer look at this interesting water adsorption phenomenon and plotted kinetic data during the transition process for the 0.2 M sample. It took ~9.4 min for the sample to respond to the increase of the environment humidity from RH 60–70%. During that time, the weight of the sample increased indicating more water adsorption at higher humidity, routinely observed in all classes of materials including carbons. However, the sample weight suddenly dropped and leveled out with time, leading to the transition point observed in the water isotherm. The ~2% weight change of the adsorbed water is actually significant because the water capacity for our sample at ~RH 90% is only 4 wt%, indicating that the water expelled reached ~50% of the adsorbed water.

Various spectroscopic and microscopic techniques were employed to characterize the rod chemistry but were inconclusive. XPS, EDS, Mössbauer, TEM, SEM, and PXRD analyses yielded interesting chemical speciation and ruled out the expulsion being a chemical event. Pore size distribution and surface area measurements from nitrogen sorption measurements (Brunauer-Emmett-Teller analysis) indicated that the rods are non-porous from their very low surface area and discovered that water is merely adsorbing to the surface of the rods forming a monolayer of water. The calculated adsorption capacity agrees with the experimental values, suggesting that the water uptake is likely proportionate to the surface area and aspect ratio of the rods. As water forms a monolayer on the rods, the only way for half of the water to be expelled is if one of the monolayers disappears. The only rational explanation for such an event would be if two adjacent rods came together and squeezed out a monolayer. We propose a mechanism where adjacent water-coated carbon rods come together through the formation of a bridging monolayer of water like a zipper propagating outward from where rods are joined and intersecting. We are currently focusing on further characterizing this unique behavior in a new project. The latest results have been prepared into a manuscript that was submitted to *Nature*.

In all, a patent and four manuscripts have been prepared from the results of this year's work. One journal article was accepted in a themed issue in *Current Inorganic Chemistry*. A second manuscript on the carbon rods has been submitted to *Nature*, while two other manuscripts were submitted to *Nano Letters*.



Materials preparation, structure, and spectroscopic imaging: a) Schematic of preparation of carbon rods; b) Scanning electron microscope (SEM) image of as-synthesized carbon rods; c,d) SEM images of carbon rod-1 synthesized at 120°C and 180°C, respectively, using 0.1 M $FeCl_3$ as precursor; e) Carbon rod-2 synthesized at 180°C using 0.2 M $FeCl_3$; f,g,h,i) STEM-energy dispersive spectroscopic (EDS) mapping of carbon, iron, and sulphur in carbon rod-1; j,k) Representative annular darkfield images of the carbon rods showing layered domains of iron clusters spaced ~2 nm apart.

PN14057/2641

Novel CO_2-Selective Polymer/Double Salt Composite Membranes for Continuous CO_2 Removal from Warm Syngas

Xiaohong Shari Li

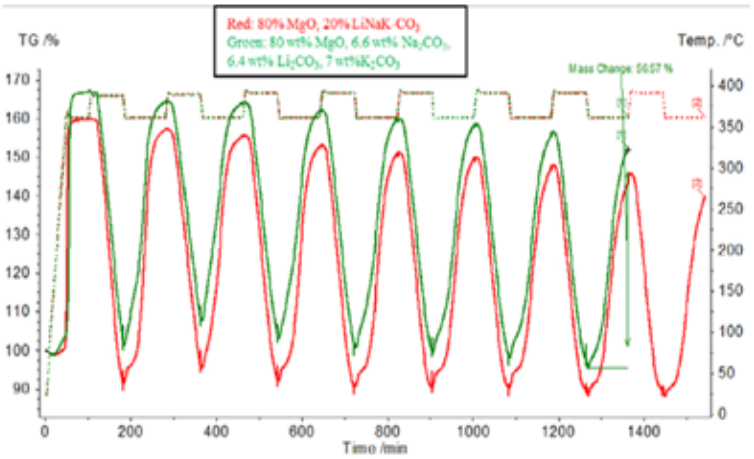
We are developing a robust CO_2-selective double salt/molten phase composite membrane for CO_2 separation from warm syngas to enhance CO conversion and H_2 recovery.

Carbon capture is critical in many fossil energy conversion processes. Current existing technologies for carbon capture from warm syngas are mostly based on solvent or adsorption-based processes that are energy intensive and require inefficient heating and cooling of the syngas stream. The membrane separation process holds promise due to its lower cost, easier scale-up, and smaller energy footprint. However, no membranes have been developed for practical CO_2 separation from warm syngas due to the limitation of existing materials.

The aim of this project was to develop a robust CO_2-selective composite membrane that can continuously separate CO_2 from warm syngas at 300–400°C using MgO-based double salts. The main challenges in membranes development are the inability to eliminate pinholes, which resulted in only modest CO_2/H_2 selectivity due to fast H_2 diffusion; and inherently slow CO_2 transport in the molten salt/double salt system. We made significant advances in materials development in FY 2014 based on the absorption/desorption approach for the capture and release of CO_2 rather than a membrane approach. In FY 2015, we proposed a scope change from the development of "CO_2-selective membranes" to "molten phase promoted CO_2 separation materials" from the progress we made during the previous year.

Our studies found that addition of $NaNO_3$, which becomes molten at the temperature of absorption and desorption, facilitates the conversion of MgO to $MgCO_3$. Triple phase boundaries (TPB) comprising the solid MgO, molten $NaNO_3$, and gaseous CO_2 are required for MgO to capture CO_2. Because $NaNO_3$ is a strong oxidizing agent, the applications of the $NaNO_3$-promoted adsorbents are limited. Thus, for FY 2015, we focused on replacing $NaNO_3$ with alternate molten salts, especially with pre-molten salt that forms a thin liquid film that can activate the MgO-based absorbent surface at the point of contact without migration. Replacement of $NaNO_3$ with a salt having higher melting point so that it is in pre-molten condition at the operation temperature is expected to improve the stability of functioning material. LiNaK-CO_3 eutectic (melting point >390°C) and LiNaK-Cl eutectic (melting point >350°C) were used to replace $NaNO_3$, and there was a comparison of TGA results from MgO + $NaNO_3$, LiK-Cl, and LiNaK-CO_3. Like $NaNO_3$, both LiK-Cl and LiNaK-CO_3 can promote MgO significantly to capture CO_2. LiNaK-CO_3 eutectic with different melting points (397°C and 498°C) was also studied. A much lower absorption rate (~10 times) appears for the sample with 498°C melting point eutectic. The observed results are consistent with the pre-melting approach; i.e., a thin liquid film formed at the salt surface due to pre-melting can also activate the MgO-based absorbent. The thickness of the liquid film is related to the temperature, or the difference between the temperature and the melting point. To understand the physical condition and the role of molten/pre-molten phase of LiNaK-CO_3 during the CO_2 absorption on MgO, differential scanning calorimetry (DSC), *in situ* FTIR, and *in situ* XRD measurements were conducted. Both *in situ* XRD and FTIR confirmed that pre-melting of LiNaK-CO_3 exists.

The preparation of LiKNa-CO_3 promoted MgO based absorbents was facilitated by forming the LiKNa-CO_3 eutectic *in situ*. The image shows the comparison of MgO with pre- made LiKNa-CO_3 and Li_2CO_3, Na_2CO_3, and K_2CO_3. Very similar performances were observed, and stable cycling CO capacity up to 13 mmol/g was achieved.



TGA cyclic CO_2 absorption-desorption results of MgO+ LiKNa-CO_3

In summary, we successfully replaced $NaNO_3$ with non-oxidizing pre-molten salts, and highly stable cyclic capacity (>10 mmol/g) was achieved. For FY 2015, we presented our results at the national American Chemical Society meeting, and as of the end of FY 2015, three manuscripts were in preparation.

PN13006/2487

Observing and Quantification of the Initial Stages of Nucleation and Growth in Liquids

Nigel D. Browning

We are examining the dynamic processes behind the synthesis and operation of energy materials that provide unique insights into structure-function relationships needed to develop and implement new energy technologies.

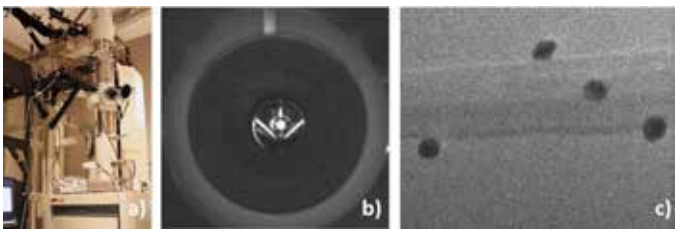
Key processes important to the synthesis and operation of next generation energy technologies involve atomic movement on the microsecond timescale or faster. Typically, the movement occurs at specific interaction locations that can be sub-nanometer in spatial extent and in complex gas or liquid environments (e.g., the electrode-electrolyte interface in energy storage technologies). We will make direct dynamic observations about these length and time scales using unique state-of-the-art microscopy methods and to use these observations to develop a fundamental understanding about how the atomistic mechanisms define the all-critical material/device performance on the mesoscale (i.e., the length and/or time scale over which a particular structure "locks in" the desired functionality).

Our research will focus on a systematic analysis of a representative set of systems that exhibit specific processes important to energy technologies. A fundamental atomistic understanding of precipitation phenomena such as the nucleation and growth of nanostructures from an aqueous solution can have far-reaching implications on new material synthesis and the design of cheap, stable, efficient batteries, research themes that align well with DOE goals. As part of our work, the unprecedented sub-μs temporal resolution of the dynamic transmission electron microscope (DTEM) will be developed to obtain a quantitative observation about the evolution of structures from individual atoms to mesoscale structures and complexes under varied environmental conditions that will be correlated with first principles modeling/simulations. These observations, including the fast transient intermediate states in each process, will provide unique insights to optimize material synthesis routes and operating parameters for advanced energy technologies.

Our work in FY 2015 focused on establishing the DTEM as a working instrument capable of time-resolved imaging. In addition, preparations have been made for nanoscale experiments that can be performed when the DTEM becomes operational. These preparations involve two sets of experiments: one, a synthesis of nanoparticles involving bimetallic core shell architectures; the other, the identification of active catalytic sites in an oxide catalyst.

One of our goals this year was to demonstrate that the DTEM could work in pulsed mode. This effort involved installing a new tip for photoemission and commissioning and aligning the laser system for photoemission. A state-of-the-art research tool, the laser system was integrated with the microscope with no pulses. The images show that the physics of the process work and the microscope can be aligned in imaging mode using both C correctors and the energy filter with a minimal loss of current down the column. The photo images are limited by the power of the laser: there are not enough electrons created in the emission process for the highest resolution image. Thus, work in FY 2016 will optimize the laser pulses for the pulsed beam generation. Given the efficiency that can be determined from the results, the pulsed beams should contain enough electrons to run the DTEM at the highest possible combination of spatial and temporal resolution.

Work to prepare samples for dynamic imaging in the DTEM has focused on materials that can be imaged both in liquid and gases. Results were obtained from two of the high resolution preparation experiments. In the first test, a core shell bimetallic particle synthesized by colleagues at the University of Miami were observed. These types of samples will be used to verify the synthesis route *in situ* and to observe the coalescence effects and solid-liquid interface structure. In the second experiment, the atomic resolution image showed a MoVTeO catalyst sample, where the goal is to observe the active catalyst sites. The DTEM experiments will use gases to water vapor to change the local chemistry and pinpoint the atomic scale interactions occurring at the solid-gas interface. Both of these experiments represent a set of processes that will be investigated using the microscope.



a) The DTEM, showing the integration of the two laser paths for stimulation of the photoemission and the specimen; b) the alignment of the photo emitter to create a beam of electrons; and c) the first CW photoemission, showing images of nanoparticles on a carbon support.

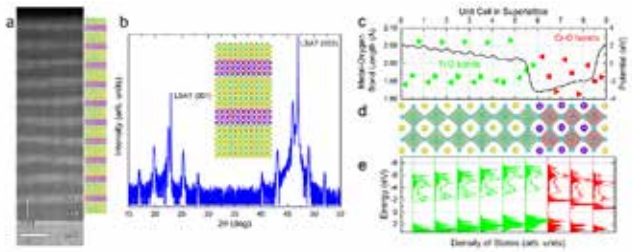
PN15013/2688

Optical Properties Modification in Complex Oxide Epitaxial Films via Alloy Formation

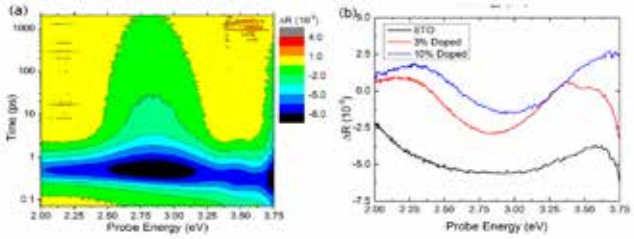
Ryan B. Comes

We are engineering the optical and electronic properties of complex oxide thin films by doping the materials to reduce the band gap and interface formation to promote separation of optically excited charge carriers.

There is great interest in finding new materials that can harvest sunlight effectively for converting photovoltaics and powering photochemical reactions. Because the solar spectrum is more abundant in visible than in UV light, finding photoactive materials that absorb in the visible is of particular importance. Many recent popular photovoltaic materials use elements that are either toxic or rare; moreover, their surfaces form oxides in the atmosphere that can alter their otherwise useful properties. An ideal class of materials for future photovoltaic applications is complex metal oxides, which are already stable in air and afford flexibility in designing and synthesizing tailored materials. Complex oxides also exhibit a wide range of optical and electronic properties. For example, $SrTiO_3$ (STO) exhibits the highest reported electron mobility of any perovskite oxide. When epitaxial strain is applied, it can be made ferroelectric, producing a built-in electric polarization to separate electron-hole pairs in photovoltaic material. However, STO has a wide optical band gap of 3.2 eV, making it a poor absorber of visible light.



Above: $SrTiO_3$-$LaCrO_3$ superlattice a) scanning transmission electron microscopy; b) X-ray diffraction; c,d,e) density functional theory (DFT) model. Below: a) time-dependent transient reflectance spectrum for $Sr0.97La_{0.03}Ti_{0.97}Cr_{0.03}O_3$ thin film; b) comparison of spectra for three films with different La and Cr doping concentrations.



In FY 2014 and FY 2015, we focused on the growth of epitaxial doped perovskite films using molecular beam epitaxy, specifically exploring the co-doped $Sr_{1-x}La_xTi_{1-x}Cr_xO_3$ (SLTCO) system. In this material, La^{3+} dopants stabilize defect-free Cr^{3+}, reducing the optical bandgap by ~0.9 eV while preserving the material's semiconducting properties. This work enables the ability to use these films for photocatalytic and photovoltaic applications because the materials exhibit visible light absorption. Ongoing work is focused on engineering the SLTCO films and related La, Cr co-doped $BaTiO_3$ system to produce ferroelectric materials for a ferroelectric photovoltaic with high carrier mobility. Photoconductivity, piezoresponse force microscopy, electronic transport, and photocatalysis measurements are being performed to understand the material properties. Using spectroscopic ellipsometry transient reflectance measurements, we were able to show that SLTCO films exhibit free carrier generation in the visible light regime as a result of the doping process. We also observed good photoconductivity response from ~2.3–3.2 eV.

Characterizing SLTCO films via X-ray absorption spectroscopy produced novel insights into film properties. Extended X-ray absorption fine structure (EXAFS) analysis showed that there may be a driving force for the dopants to occupy the nearest neighbor sites, contrary to what was previously predicted theoretically. Modeling via DFT confirmed that the atomic layer-by-layer film growth process promotes this type of dopant coupling, even though it is not expected to occur in bulk synthesis. This result enhances understanding of the epitaxial oxide thin films growth process.

Work during FY 2015 expanded to include $SrTiO_3$-$LaCrO_3$ superlattice films. By tailoring the growth process, we showed that ferroelectric polarization is induced in these superlattices by the positively and negatively charged interfaces in the materials. This finding represents a breakthrough in engineering the properties of complex oxide thin films. Through EXAFS and electron microscopy measurements as well as DFT modeling, we built a detailed understanding of the phenomena that occur in these materials. Ongoing work is focused on measuring the polarization using synchrotron X-ray photoelectron spectroscopy, allowing us to examine the electronic properties of individual layers of the superlattice, never before performed in this level of detail. The polarization in these materials may be used to separate electron-hole pairs generated at the interfaces by optical excitations, making our superlattices useful for photovoltaic and photocatalytic applications.

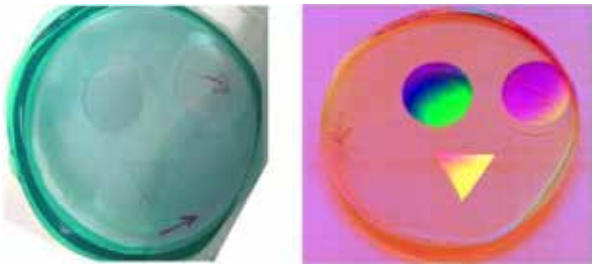
PN13100/2581

Optically Resonant Subwavelength Films for Tags and Seals

Kyle J. Alvine

We are developing a counterfeit-resistant, tamper-indicating film critical to identifying potential security breaches for arms control and treaty-accountable tracking applications.

There are multiple applications in the transport and handling of nuclear materials in which counterfeit-resistant tags and seals that incorporate tamper indication are critical to identifying potential security breaches. These may include multiple tamper applications such as tags and seals with counterfeit and tamper-indicating properties for UF_6 cylinder tracking. While different applications may have unique requirements, the tags and seals require tamper indication and a unique signature to prevent counterfeiting.



Comparison of a photograph of a patched subwavelength film (left) to a resultant image from PCA of a polarized hyperspectral image. The smaller circles and triangles are the nanostructured films in a surrounding material. Both the patching and misalignment of the nanostructured patches is readily apparent in the PCA image.

In this project, we are studying and demonstrating proof-of-concept tamper indication performance of newly-developed subwavelength films that are particularly well suited to applications in tags and seals. These films have a unique optical signature that is wavelength, angle, and polarization-dependent and can be tailored to operate in a broad wavelength range from the visible to the infrared region. Potential applications include tags or seals for UF_6 cylinders. We expect to demonstrate tamper indication and unique signatures for counterfeit resistance for common tampering mechanisms (cutting, peeling, and tearing) in a subwavelength film.

During FY 2014, we began preparations for the fabrication of test samples to investigate tamper indication routes early in the next fiscal year. We also began work on a scalable coater to prepare larger samples eventually after initial testing on the 2-inch samples. For FY 2015, we prepared a large number of 2-inch coupon films for tamper testing. This sample set included varied fabrication parameters for later comparison tests. Preliminary optical testing on the samples showed the expected resonant optical response. In part, the large number of coupons was prepared to guard against possible delays in the next year from an anticipated laboratory relocation. We have a large enough stockpile of samples to avoid any delays throughout the next year, and we have used several of these samples to complete tamper indication testing, which includes cutting of lines and holes, material replacement, material substitution, peeling, and heating. Color matching of substitute material was also accomplished for more realistic tests.

Hyperspectral imaging was used both to investigate tamper detection on our samples and to aid in the design of an eventual (simple) reader for the films. Hyperspectral imaging collects the spectral response of the sample in the visible range at each pixel in the image, rather than just red, green, and blue information. Principle component analysis (PCA) is then used to look for correlation and contrast in the image from different wavelength regions. With hyperspectral imaging, we were able to locate and identify cut marks that were difficult to find via simple visual inspection. Patching was even more apparent: nanostructured films stood out with high contrast compared with color-matched fill material under hyperspectral PCA. When polarization was added to the hyperspectral setup, independent comparative rotation of the nanostructured film sections was readily apparent. These results are highly promising for tamper indicating.

During FY 2015, we had promising results in tampering and counterfeit detection of subwavelength films prepared in the project. Holes, cuts, and color-matching replacements were examined with hyperspectral imaging as a function of wavelength and polarization. To avoid any project and progress delays, we have been more recently focused on preparing a significant number of subwavelength samples for testing to avoid conflicts. Some of these findings were presented at an international conference, and a peer-reviewed publication is currently in preparation.

In FY 2016, we will continue performing tamper testing of materials with a focus on adhesive films. Further testing will be done with peeling and potential thermal damage. In addition, we will investigate further damage-related mechanisms by including strain inducing polymer films and oxidizing metals into the nanostructured samples. Further development of a simple reader and the preparation of larger scale samples for testing will also be performed.

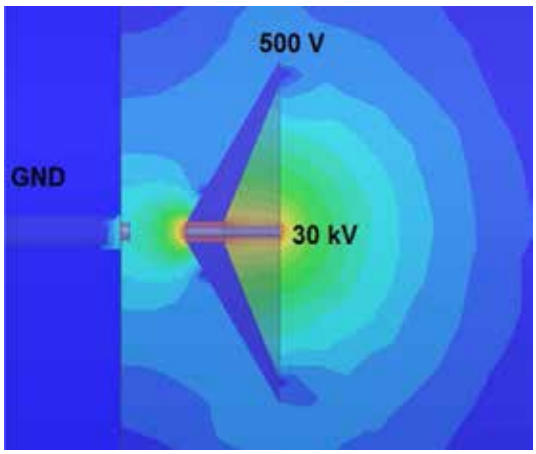
PN14090/2674

Optically Stimulated Luminescence Data Storage

David W. Gotthold

We are developing a new approach for data storage using optically stimulated luminescence (OSL) that can be scaled to high data densities with excellent data lifetime and integrity.

To meet the ever-increasing data storage need for cloud computing, scientists and engineers are constantly pushing the limit of data storage density. Hard disk drive (HDD) has been the dominant computing data storage device for the past 50 years, with over 800 million units sold in 2012. Until recently, HDD density increased by 100% every year, but advancing technology has now decreased this rate to 25%. Solid-state hard drive (flash) is the storage method based ferroelectricity, where direct wiring enables immediate access to the bit. However, flash suffers memory wear; thus, it can be used only as short-term storage. Although CD, DVD, and Blu-ray are popular optical data storage methods, they have a significantly lower density (<10% of HDD). Still another recent advanced storage method is holography, a promising technology with its large density and fast data access rate, reading a page each time instead of a bit (like flash). However, sensitivity to vibration and extremely low speed have prevented this technology from succeeding.



Model of the electric field around the photocathode in the JEOL 5900 SEM.

We propose to develop a new data approach capable of making a paradigm change in storage technology. OSL has been in use for several years as a radiation dosimetry technology. OSL media has an extraordinary linear optical response (over eight orders of magnitude for lithium fluoride [LiF]) that will enable ternary (higher level) encoding of data in a single bit, thus storing more data in each defined location. The objective of this project is to prove the concept of OSL data storage by demonstrating multi-values data encoding. This information is a primary concern for potential development partners and will be key in identifying the potential market opportunities for this new technology.

Based on work done in previous years, the lack of knowledge about the OSL process at high power levels is identified as the critical technology gap. To address this issue, a new project commenced to develop a short pulse electron source capable of producing the ionizing radiation at and energy density and pulse length necessary to evaluate the dynamic formation of the F-centers responsible for the OSL signal. To measure OSL center formation, a high energy pulse source of ionizing radiation needed to be developed. After evaluating a range of options including pulse X-ray, gamma and electron beams, we determined that a variable intensity electron beam would be the easiest to generate and control; therefore, development work in FY 2015 has focused on building a picosecond pulsed electron beam source with variable intensity.

To achieve the targeted short time high intensity pulses, a laser pumped photocathode was determined to be the best approach, and the design and build of this system has been the focus this year. Based on prior work developing a dynamic transmission electron microscope, a laser driven photocathode system is being developed. This system will be integrated with an existing scanning electron microscope to enable the focusing of the electron pulse and control of the energy density. The drive laser is a Fianium HYLASE with a frequency quadrupling crystal system to provide a 266 nm pulse that will be directed into the scanning electron microscope (SEM) column and onto a tantalum photocathode. The field energies around the photocathode and along the SEM column were to understand the pulse energy propagation through the system. In addition, F-centers are strongly influenced by crystal defects and grain boundaries. By growing the LiF films under different process parameters, we can quantify this relationship and generate predictive tools.

In FY 2016, the system build will be complete, and LiF samples will be exposed at a range of pulse energies and speeds to probe the F-center formation process. This procedure will enable a more complete understanding of the nature of the OSL effect, formation of F-centers, and limitations of dose rate for this material. We will also have a high speed pulsed electron source coupled with an SEM that is expected to be useful for probing a range of ultra-fast processes in critical areas such as catalysis, structure evolution in lightweight alloys, and battery electrodes.

PN15081/2756

Oxygen Sensors by Plastic Impregnation Using Solvent Immersion Methods

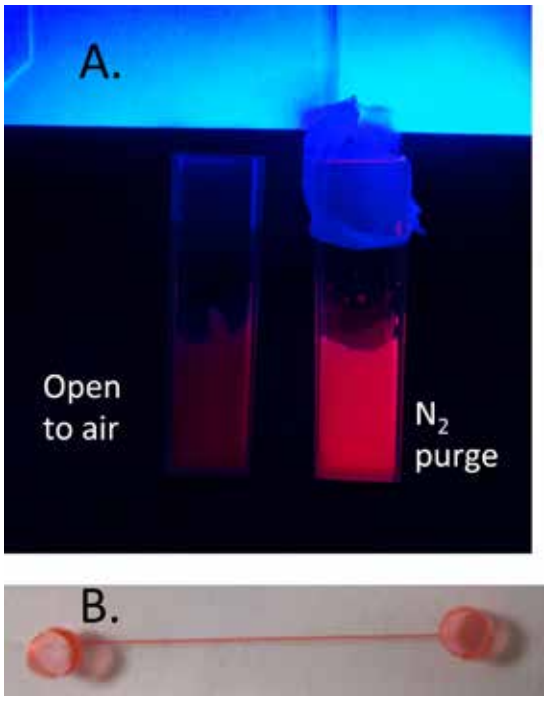
Jay W. Grate

This project is developing a new methodology for dissolved concentrations to advance the state-of-the-art in oxygen sensing.

Oxygen is among the most important electron acceptors in biology, with concentrations and gradients influencing or controlling many biotic processes in the environment. Oxygen concentrations and gradients play an important role in the growth of microbial communities in natural environments and in model cell cultures in spatially structured microenvironments. Accordingly, the ability to measure oxygen concentrations is important for research and technological purposes in point sensor and chemical imaging formats. Oxygen concentrations can be measured optically using fluorescent sensors known as optodes that contain an oxygen sensitive fluorophore in polymer or sol-gel films.

Fluorescent oxygen sensing and chemical imaging have been demonstrated previously in a variety of formats, including measuring oxygen gradients in sediments in which oxygen is microbially depleted using planar optodes for 2D imaging: imaging oxygen depletion by biofilms in planar flow cells; measuring non-invasive oxygen concentration in cell cultures; observing oxygen sensing within microfabricated wells for single-cell oxygen consumption; developing oxygen controlling microfluidic structures; and determining oxygen concentrations in such microfluidic devices for microbial or mammalian cell culture. In addition, we are developing methods to incorporate oxygen sensors into pore network microfluidic devices based on silicon and glass. Preparing such sensors entails the deposition of dye-containing film materials on an optical substrate.

In this project, we developed a novel way to alter the surfaces of plastic materials in technically useful ways using a solvent immersion technique. The contact between a solvent and the plastic surface creates a discrete gel layer by a process known as Case II sorption. This seemingly simple technique can be used to impregnate a surface layer with sensing dyes. The thickness of the discrete softened layer depends on the polymer, solvent, temperature, and length of immersion. The rate of increase of the gel layer thickness is expected to be linear with time to a first approximation. When an oxygen sensing fluorescent dye is included in solution with the solvent that creates the gel layer, the polymer surface becomes impregnated with dye to a discrete depth. After drying, this dyed layer is part of the bulk plastic but is localized at the surface and serves as an oxygen sensor. We are advancing this capability by investigating polymers, solvents, and dyes to improve the fabrication of fluorescent oxygen sensors. We are also showing the impregnation of 3D structures with oxygen sensing dyes.



A. Two cuvette structure in polystyrene, each impregnated with an oxygen sensing dye that luminesces red in the absence of oxygen, as seen under UV light, that excites the dye. The cuvette purged with nitrogen is bright while that containing air is dim, demonstrating oxygen sensitivity of the internal surfaces of the cuvette; B. A microchannel whose internal surfaces have been impregnated with the oxygen sensing dye, as seen under white light.

Polystyrene was impregnated with oxygen sensing dye using solvents and solvent mixtures. While acetonitrile at room temperature is very slow to impregnate and may not impregnate dye to the same depth as the solvent gel layer penetration, we found that raising the temperature to 50°C or adding acetone as a cosolvent greatly improved the efficiency of the dye impregnation. The interiors of polystyrene cuvettes and microchannels in polystyrene were successfully impregnated by these methods and shown to be oxygen sensors.

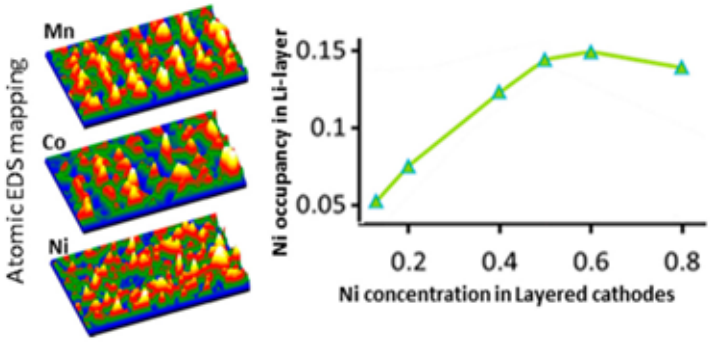
PN15067/2742

Probing Structure-Property Relationship of Energy Storage Materials Using *Ex Situ* and *In Situ* Dynamic Microscopy and Spectroscopy with High Spatial and Fast Temporal Resolution

Chongmin Wang

We are probing the structure-property relationship of next generation energy materials to enable accelerated discovery of new materials for energy security and sustainability.

Electrochemical energy storage devices such as lithium (Li)-ion, Li-S, Li-O, Na-ion, and multi-valence ion batteries are complex multi-component systems that incorporate widely dissimilar materials and phases in physical and electrical contact. Despite the success of Li-ion batteries, there are at least four areas in which new research and development progress is needed: higher storage capacity; more rapid charging; increased cycle life, and discovering a new energy storage media. The goal of our research is to develop and use imaging, spectroscopy, and tomography methods to probe the structural and chemical evolution of energy storage materials with atomic spatial and fast temporal resolution to determine the structure-property relationship and its correlation with charge and ion transport in energy materials. In particular, these methods will explore the new chemistry and nanostructured materials for energy storage by developing chemical imaging methodologies based on *ex situ* and *in situ* transmission electron microscopy, scanning transmission electron microscopy (STEM), dynamic transmission electron microscopy, electron energy loss spectroscopy, energy-dispersed X-ray spectroscopy, scanning transmission X-ray microscopy, X-ray tomography, and nuclear magnetic resonance (NMR).



Atomic resolution STEM-EDS mapping to quantify the migration of Mn, Ni, Co towards the lithium layer in layer structured lithium transition metal oxide as cathode for Li-ion batteries.

In FY 2015, we captured direct atomic resolution visualization of interatomic layer mixing of transition metal (Ni, Co, Mn) and Li ions in layer structured oxide cathodes for Li-ion batteries. Using chemical imaging with aberration corrected STEM and density functional theory (DFT) calculations, we discovered that in the layered cathodes, Mn and Co tend to reside almost exclusively at the lattice site of transition metal (TM) layer in the structure or little interlayer mixing with Li. In contrast, Ni shows high degree of interlayer mixing with Li. The observed distinctively different behavior of Ni with respect to Co and Mn provides new insights on both capacity and voltage fade in this class of cathode materials based on lithium and TM oxides, therefore providing scientific basis for selective tailoring of oxide cathode materials for enhanced performance.

Another major achievement was the innovative development and the first-time use of *in situ* liquid secondary ion mass spectroscopy (SIMS) for probing the solid electrolyte interphase layer in rechargeable battery. Dynamic structural and chemical evolution at solid-liquid electrolyte interface is always a mystery for a rechargeable battery due to the challenge to probe a solid-liquid interface directly under reaction conditions. We discovered that the deposition of Li metal on copper electrode leads to the condensation of solvent molecules. Chemically, the layer of solvent condensate tends to be depleted of the salt anions and with reduced concentration of Li^+ ions, forming a layer adjacent to the electrode and contributing to the over-potential of the cell. This observation provided unprecedented molecular level dynamic information on the initial formation of the solid electrolyte interphase layer. Ultimately, this work opened new avenues for implanting the *in situ* liquid SIMS concept to probe the chemical reaction process that intimately involved solid-liquid interface such as electrocatalysis, electrodeposition, biofuel conversion, biofilm, and biomineralization.

PN13010/2491

To address the capacity and voltage fading of cathode materials, we studied in detail of the model material Li_2MnO_3, a major challenge for the application of this category of material and believed to be associated with the structural and chemical evolution of the materials. This work gives the detailed structural and chemical evolutions of Li_2MnO_3 cathode captured by using aberration corrected STEM after a certain number of charge-discharge battery cycling. It was found that structural degradation occurred from the very first cycle and was spatially initiated from the particle surface propagated toward the inner bulk as cyclic number increase, featuring the formation of the surface phase transformation layer and gradual thickening of this layer. The structure degradation followed a sequential phase transformation, monoclinic C2/m → tetragonal $I4_1$ → cubic spinel, consistently supported by the decreasing lattice formation energy based on DFT calculations. For the first time, high spatial resolution quantitative chemical analysis revealed that 20% oxygen in the surface phase transformation layer was removed, and a Li-depleted layer with reduced Mn cations developed. This work demonstrated a direct correlation between structural and cell's electrochemical degradation, enhancing our understanding of Li-Mn-rich cathode materials.

In the new chemistry for batteries, we collaborated with GM Global Research Center and studied the Li-S system in detail. The Li-S batteries are promising candidates for portable and large-scale energy storage; however, the poor stability of polysulfide species during battery cycling is a challenge that severely hampers this technology. The instability leads to the "shuttle phenomenon" in which the polysulfide molecules dissolve and diffuse to the Li electrode, causing dendrite growth through parasitic reaction. The difficulty in addressing this issue originates from the gap between battery material synthesis efforts and current knowledge about the molecular structure and stability of dissolved polysulfide species. To unravel the structure and possible stability related reactions of polysulfide species, DFT, magnetic resonance, and X-ray spectroscopy studies were performed for the Li-S system. Multinuclear NMR, variable temperature electron spin resonance, and sulfur K-edge X-ray absorption spectroscopy analyses revealed that the Li exchange between polysulfide species and solvent molecules constituted the first step in the dissolution process, leading to de-lithiated polysulfide ions (Sn^{2-}) and subsequently forming highly reactive free radicals through dissociation reaction (Sn^{2-}---$2S_{n/2}$). The energy required for the dissociation and possible dimer formation reactions of the polysulfide species was analyzed using DFT calculations. Based on these findings, we discussed approaches to optimize the electrolyte to control the polysulfide solubility.

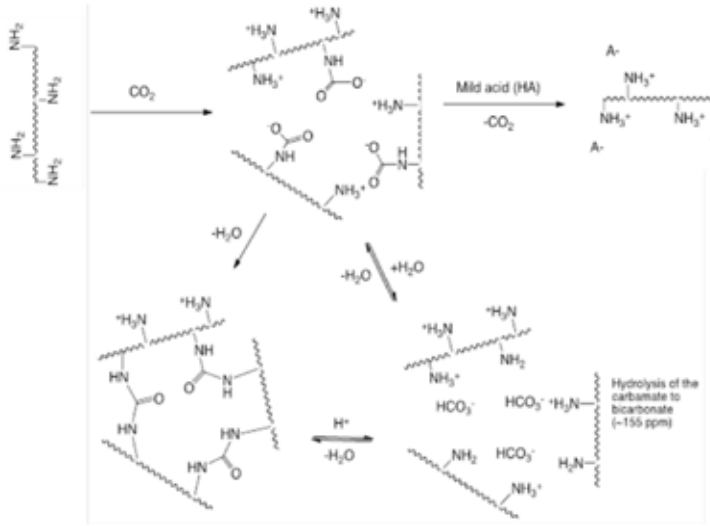
In total for FY 2015, this project produced five peer-reviewed journal publications, four invited talks, and five conference presentations. At the same time, the lead author has been heavily involved in the focused research group activity of high capacity anode material based on Si. At project conclusion, we will continue our efforts by using *in situ* and *ex situ* imaging methods to study Li-ion, Li-S, and multi-valence ion batteries, all crucial for energy storage. We will integrate different capabilities and theoretical calculations closely and collaborate with research efforts of JCESR, DOE, and other projects and industrial organizations to elevate energy storage research efforts for scientific and industrial applications.

Rheoreversible CO_2-Reactive Hydraulic Fracturing Fluids for Unconventional (Tight) Oil Production

Carlos Fernandez

This project is demonstrating the potential of a technology to enhance permeability cost effectively in oil and gas reservoirs while minimizing environmental impact.

Activated at certain reservoir depths, CO_2-promoted crosslinking reactions can promote rapid volumetric expansions and increase mechanical stress in constrained environments. In this fashion, it will be possible to maximize the efficiency of hydraulic fracturing operations for tight oil production while decreasing environmental impact. Ultimately, this technology will reduce U.S. dependence on imported oil and contribute to the national economy by enhancing fracture permeability, decreasing water usage for fracturing, and potentially aiding in oil recovery. This work reports on the chemical mechanism responsible for the volume expansion of polyallylamine solutions reacting with CO_2 at temperatures relevant to unconventional oil and gas reservoirs. It demonstrates the potential recyclability of the fluid upon depressurization due to the rheoreversible behavior of the expansion. Finally, the chemical stability of the polymer is evidenced upon recycling, suggesting that these fracking fluids are greener, cost-effective alternatives to conventional fluids for reservoir stimulation and fossil fuel production.



Conceptual reactive polymers "gelling" in the presence of CO_2.

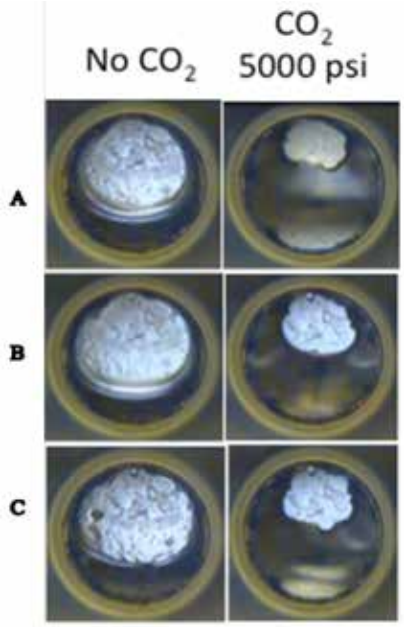
The hydraulic fracturing processes utilize large volumes of fluid (million gallons of water per well), chemicals, and proppants that are pumped down the wellbore at high pressures to create a network of cracks in the reservoir rock. Previous work demonstrated that non-toxic CO_2-expanded fracturing fluids developed for stimulation of high temperature geothermal environments could be extended to low temperature reservoir stimulation dramatically enhancing the permeability of crystalline rock materials as compared to current technology. Under pressure and temperature conditions (40°C–130°C; 5,000–10,000 psi) of certain tight oil plays (for example Avalon/Bone Spring and Monterey/Santos plays) where the polymer and water are delivered in a constrained space, the addition of CO_2 can induce abrupt crosslinking and curing of the gel promoting in this mode a rapid increase in hydrostatic pressure due to the large volumetric change occurring at the reservoir. CO_2-triggered volume expansion experiments showed that environmentally friendly amine-based polymers; polyallylamine (PAA, MW=17K and 65 K Dalton), polyacrylamide (PAC, 40K D) and polyethylinimine (PEI, 750K D); all introduced volume expansions of up to two times the original volume at pressures as low as 2000 psi. Variables including CO_2 pressure, pH, polymer concentration, and molecular weight may be used to adjust the volume expansion and the stress originated in confined environments as a result of this volume changes. In this regard, the chemical mechanism involved in the reaction of CO_2 with aqueous polyamine solutions was studied at temperatures relevant to tight oil reservoirs. The potential recyclability of the polymer solutions was also investigated and the stability of the polymers analyzed after a number of cycles where the polymer solution transitioned to an expanded fluid and reverted back to a polymer solution upon CO_2 pressurization/depressurization.

The proposed reaction mechanism between CO_2 and polyamines was demonstrated, where a carbamate intermediate if formed upon association with CO_2 followed by a dehydration reaction and the formation of a urea linkage. To verify,

PN15048/2723

high pressure/high temperature magic spin angle (MAS) ^{13}C NMR was performed using rotor technology developed at EMSL on two candidate polymer solutions that undergo volume expansion at temperatures relevant to tight oil/gas reservoirs (40–130°C), PAA (MW=17K Da) and PAC (MW=40K Da), which showed volume expansions of up to two times the original volume at 50°C and 100°C and CO_2 pressures between 3500 and 5000 psi. CO_2 reaction with PAA generates a broad peak resulting from the overlap of a peak at 158 ppm and a second peak at 161 ppm corresponding to carbamate and urea functionalities co-existing at 4000 psi of CO_2. Experiments on PAC solutions with higher concentration will follow.

The rheorevesible nature of the CO_2-triggered volume expansion process of the polymer solutions was studied to learn about the potential recyclability of the fluids during reservoir stimulation under unconventional oil/gas environments. The image shows the results of high-pressure experiments on a HP transmission view cell, where a 1wt% PAC (MW=40K Da) aqueous solution is subjected to incremental pressures of CO_2 up to 5000 psi followed by partial depressurization to 1000 psi. The increase in solution volume level when pressurized with CO_2 is followed by a decrease of the volume level upon depressurization. Additionally, there is a process can be performed multiple times to demonstrate the potential recyclability of polymer solutions upon depressurization.



HP rheology experiments on a pressurized transmission view cell. Images A, B, and C are three separate tests where the same PAC (MW=40K Da) 1wt% aqueous solution was pressurized with CO_2 followed by partial depressurization to 1000 psi. The results show complete reversibility of the expansion process as seen by the reversible increase in the polymer solution level.

Experiments carried out with PAA (MW=65K Da) at both 50°C and 100°C ratify the reversibility independently of the type of functionality (amine or amide). This result provides evidence that a cross-linking reaction with PAC is occurring, even though HP NMR did not show the chemical functionality at the concentrations at which the experiment was performed. Finally, ^{13}C analysis of a PAA solution after cycling CO_2 pressures was performed that showed no indication of polymer degradation after three cycles, verifying the stability of these fluids upon recycling.

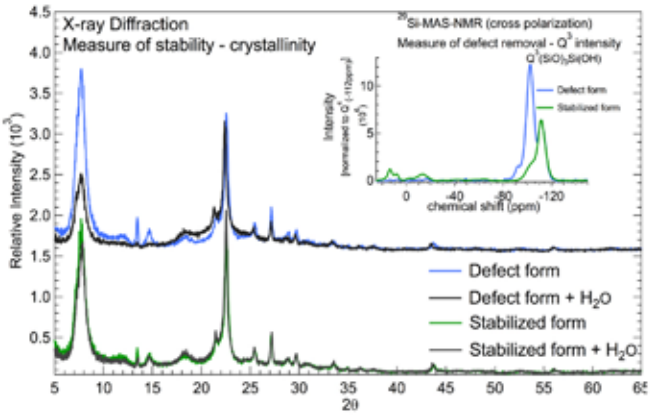
Robust Hierarchical Zeolite Frameworks

Miroslaw A. Derewinski

This project provides a molecular description on the formation and arrangement processes during microporous crystalline silicate synthesis using PNNL's advanced measurement capabilities and uses that knowledge to synthesize nano-sized and mesoscopically structured zeolites with tailored chemical and textural properties.

Modern industrial processes focusing on catalysis, phase separation, or ion exchange are becoming increasingly dependent on the superior qualities of molecular sieves based on Si-Al and Si-Al-P. Their structural versatility, robustness, and chemical properties are beneficial to facilitating most methods. By tailoring these properties, upgrading processes such as biomass conversion reactions and exhaust treatments becomes attainable. Specifically in this project, we are focusing on and gaining important insights in understanding the role of structural defects and prevention of such, affecting the stability of zeolitic material in hot liquid water; exploring the formation mechanism of zeolite structures using Al as a probe molecule and *in situ* spectroscopic methods; and reducing the size of zeolitic particles and embedding them in mesoporous lamellar structures to enhance transport phenomena and thus increase catalytic activity.

This project is yielding information on synthesis and post-synthesis approaches that enable preparations of new, more stable, and active zeolite-based materials. We investigated low zeolite stability in liquid water phase at elevated temperatures, a significant weakness of most solid acid zeolites that limits their applicability in typical biomass conversion reactions. Stability depends on the concentration of structural defects such as hydroxyl nests, a cluster of four Si-OH groups within close proximity. Previously synthesized high silica zeolites isomorphously substituted with boron generated a model system enriched with structural defects. We showed conclusively zeolite liquid water stability is dependent on the number of defects. Their longevity in hot liquid water, a desired property for use in processes such as hydrodeoxygenation of lignin-derived molecules occurring in the aqueous phase, can be significantly increased via selective removal of structural defects by employing a modified version of commonly used silylation methods with chloroalkylsilanes.



X-ray diffraction (XRD) pattern and embedded 29Si-magic angle spinning-nuclear magnetic resonance (NMR) spectra, illustrating the structural defect removal and subsequent improved stability as measured by retention of XRD crystallinity of zeolite BEA.

These promising results inspired us to focus on further optimizing the defect removal process. The use of different silylating agents is being investigated, their varying levels of reactivity hopefully giving rise to more effective silylation without the loss of activity. Application of this newly developed approach on commercial catalysts and catalysts synthesized and modified in house for biomass conversion reactions and exhaust treatments is currently underway and will be continued in FY 2016. Another promising application for these silylated materials could be in the CO_2 separation and sequestering processes, exploiting a potentially enhanced selectivity for non-polar molecules in aqueous solutions.

Another thrust in FY 2015 was tackling the zeolite formation mechanism. Using Al as a probe molecule, unique PNNL capabilities such as *in situ* NMR employing unique rotors withstanding high pressures and temperatures were exploited to investigate a high silica ZSM-5 and low silica Y zeolite. *In situ* extended X-ray absorption fine structure (EXAFS) measurements were taken at the Paul-Scherrer-Institute's Swiss Light Source in Switzerland, *ex situ* formation kinetics assessed with X-ray diffraction, and *in situ* NMR all led to new conclusions, suggesting that the environment of Al T-sites can be set at an early stage in zeolite crystalline structure formation. Additional experiments on *in situ* monitoring kinetic of zeolite Y synthesis will occur in FY 2016.

Having previously prepared stable colloidal suspensions of zeolitic nanostructures (~5 nm in diameter, XRD amorphous) subsequently assembled into mesoporous layered structures, they were tested in low temperature liquid phase isomerization of N,N'diphenylmethylenediamine to methyldianiline, an important starting material for polyurethane synthesis. New lamellar structures showed superior catalytic performance compared to other mesoporous materials. Active acid sites of comparable strength to that of zeolites, these new materials provide enhanced active site accessibility, resulting in reduced residence times of the reactants and limiting secondary reactions. In FY 2016, we will continue our study on the use of materials containing protozeolitic species as effective catalysts for liquid phase hydrocarbon transformation.

PN14026/2610

Scale-up of New Chemistry Batteries for Transportation and Stationary Applications, Material Synthesis and Pouch Cell Development

Yuyan Shao

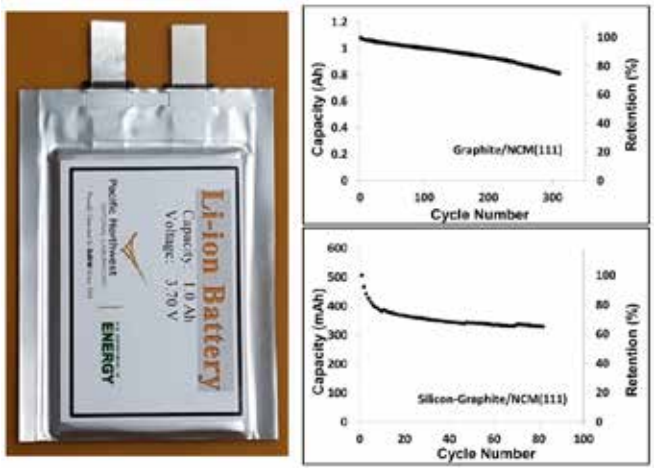
This project successfully demonstrates a baseline battery chemistry (graphite/ $Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$) and a new battery chemistry (silicon-graphite/ $Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$) in pouch cell configuration using the PNNL Advanced Battery Facility (ABF).

In March 2015, the ABF facility became operational with the purpose of investigating the scalability of advanced battery materials from coin cell to pouch cell format. To transition new battery chemistries to the market, they must be shown to work on the lab scale, and the pouch cell format is favorable due to the higher energy density and lower design cost. There are many scientific and engineering challenges that can arise when scaling up the slurry synthesis, from milligrams to kilograms of material and factors such as mixing time, temperature, concentration, and velocity to be considered. In FY 2015, we demonstrated the ability to produce high quality battery materials in the gram and kilogram scale and successfully cycled up to 1 Ah capacity pouch cells for more than 300 cycles.

To baseline the system, a traditional battery chemistry was employed in which $Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$ (NCM-111, BASF) was used as the cathode and graphite (natural spherical graphite, superior graphite) as the anode. Material synthesis and slurry mixing is done in an ambient lab using two different mixing machines. To characterize new slurry composition, it is useful to have a smaller sample size (200 g) for which we employed the THINKY MIXER ARE-310. A 6 L capacity planetary mixer is used to mix slurry quantities in the kilogram scale in which mixing can be done under static vacuum prior to slurry coating.

The electrode coating and pouch cell assembly is done in a climate controlled dry room with a dew point <40°C. The electrode coating machine is a roll to roll process that can coat the electrode film in a continuous stripe or pattern format. A 2 m two-zone temperature oven dries the film, after which time the reverse side can receive double-side coating. After calendaring and punching the film, it is further dried in a vacuum oven before wrapping the separator between opposite electrodes in a stack format. The stacking machine can be programmed to the amount of electrodes necessary, such that the number double-side anode=n, double-side cathode=n-1, and two single-side cathodes for the top and bottom. An ultrasonic welder is used to attach tabs and then the stacked cell is placed in a formed pouch for sealing and electrolyte injection. A small pocket is left in the pouch to allow space for gassing during the formation cycles.

Several 1 Ah graphite-NCM cells were made and cycled with an Arbin battery tester BT-2000 in an environmental chamber at 25°C. The cathode composition consisted of 96% $Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$ (NCM-111, BASF), 2% carbon black (superP li, timcal), and 2% PVDF. The anode electrode is comprised of 94.5% graphite (natural spherical graphite, superior graphite), 4.5% PVDF (solef PVDF, solvay), and 1% carbon black (superP Li, timcal). These cells were cycled at C/3 rate between 3.0–4.3 V with a constant voltage charge at 4.3 V until the current is below 0.05 mA. After 300 cycles, the coulombic efficiency is more than 99.6%, with capacity retention greater than 76%.



Pouch cell and its cycling performance. Baseline: graphite/ $Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$ (NCM-111); new chemistry: silicon-graphite/$Li_{1+x}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{1-x}O_2$ (NCM-111).

Preliminary work was performed on new battery chemistries such as silicon anode.

PN15008/2683

For this work, silicon particles were substituted into the graphite slurry for a total of 5% silicon (silicon powder, alfa aesar), 89.5% graphite, 4.5% PVDF, and 1% carbon black. The silicon-graphite anode was matched with the NCM cathode described above with an expected capacity of nearly 500 mAh. Capacity fading and low coulombic efficiency is seen during the first 10 cycles before it starts to stabilize. On the 80th cycle, the capacity retention is over 65% and coulombic efficiency is at 99.6%. Based on the 10th cycle, the capacity retention is ~84.5%. The expansion of silicon is a cause for concern when cycling Si-Li-ion batteries because silicon can experience a 3–4 time volume change. An increased amount of silicon will be tested in the future because minimal expansion was observed with the 5% silicon anode.

Another new battery chemistry studied in the pouch cell facility is the novel sulfur Li-ion cell. Traditionally, sulfur cathodes are paired with lithium metal, but there are safety concerns with dendrite growth during cycling. This novel cathode material as well as electrolyte composition allows lithiated graphite to be utilized as the anode. A double-side coating of more than 1.5 m was done with electrode coater and several pouch cells were cycled. Further work must be done to characterize this system in the pouch cell format.

In FY 2016, we will continue to use the ABF for scalable synthesis of new and advanced electrode materials and evaluation of these materials in pouch cells.

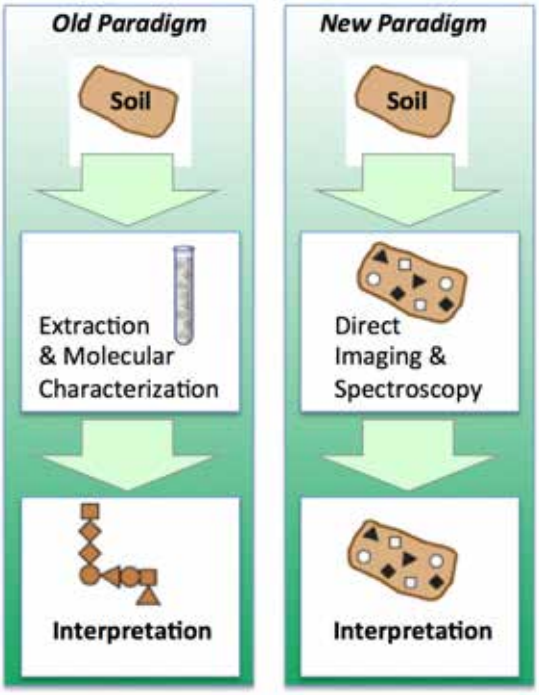
Soil Organic Carbon/Mineral Association and Aggregation Processes

Jay W. Grate

The stabilization of organic carbon in soils is critical to understanding how terrestrial ecosystem processes relate to global atmospheric carbon levels. A new paradigm relates soil organic carbon stability to its interactions – the subject of this research – with soil minerals.

Soil organic matter represents an important pool of carbon in the global carbon cycle. The annual net change in CO_2 concentration in the atmosphere represents a small difference in yearly numbers; as a result, a modest change in the behavior of one carbon pool, leading to a change in one of those large numbers (fluxes), can have a significant effect on atmospheric CO_2 levels. Accordingly, even a moderate shift in soil organic carbon persistence could significantly offset anthropogenic CO_2 in the atmosphere. Given the importance of soil carbon persistence and current knowledge gaps, the application of advanced analysis and imaging capabilities at PNNL to the interfacial chemistry of organic carbon/mineral associations in an abiotic investigation using *in vitro* model systems offers rich territory for original and impactful science relevant to DOE programmatic priorities.

This project seeks to provide a molecular-to-micron scale mechanistic understanding about how organic compounds interact with natural mineral surfaces and within aggregate structures. These issues are highly relevant to the stabilization and dynamics of soil organic carbon in terrestrial ecosystems. Contrary to the past belief that the molecular structures of carbon compounds condensed into macromolecules determined their stabilities in soil, it is now believed that the interactions of organic compounds with mineral surfaces and in aggregates of mineral particles determine the bioavailability of soil organic carbon for breakdown by biotic processes. The previous understanding was based on the extraction and organic characterization methods, while current methodology is based on actual direct observation of soil organic carbon by imaging and spectroscopy *in situ*. The latter methodology has shown that organic matter is present in organo-mineral aggregates. Accordingly, these interactions and their influence on aggregate formation are highly significant yet difficult to study at molecular or nanoscopic scales directly in soil, a heterogeneous opaque material.



Contrasting views of soil organic carbon.

We have been using a bottoms-up approach based on minerals and organic compounds with known functionality to establish an environmentally relevant model system for exploring organic-mineral interactions and aggregation processes. This project will investigate organic carbon/mineral interactions to determine which specific classes of organic compounds interact with which specific types of minerals and particles and their binding strengths; determine when and how these associations between organic molecules and mineral surfaces lead to forming primary aggregate structures; and image aggregate formation dynamically at the molecular and nanoscale in abiotic model systems using *in situ* transmission electron microscopy (TEM) methods.

Several minerals (kaolinite, mica, montmorillonite, goethite) have been obtained and were characterized (TEM, X-ray powder diffraction, atomic force microscopy, and total organic carbon measurement) to verify their identity, purity, and suitability for experiments. Using dynamic force microscopy (DFS), binding energies between selected organic molecules and mica were measured, revealing trends in molecular-scale phenomena. The free binding energies from highest to lowest on mica of various functional groups are as follows: carboxyl, amine, methyl, and phosphate.

The methodology for our model system approach has been established, demonstrating the feasibility of incorporating additional soil minerals and soil aqueous phase relevant cations. In addition, synthetic iron oxide and natural mica particles have been observed in the liquid cell of *in situ* TEM, a methodology that will be used in the next year to investigate dynamic aggregation processes mediated by organic molecules.

PN15068/2743

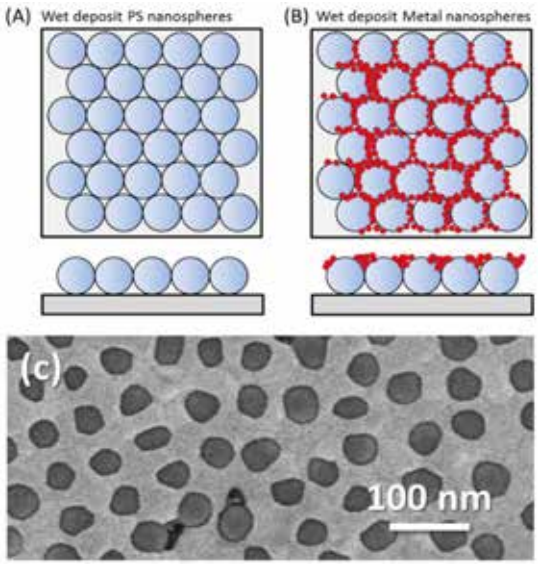
Sub-wavelength Paint with Tailored Visible and Infrared Light Scattering for Energy Applications

Kyle J. Alvine

We are developing a lower cost "wet deposition only (paint-like)" methodology for the fabrication of nanostructured subwavelength coatings on larger scales.

The nanostructures in the films under development are smaller than the wavelength of light and allow a unique beneficial scattering not possible with classical optical coatings. For example, this distinctive scattering may be used in the future for daylight control or infrared thermal management for window coatings. To our knowledge, wet deposition only manufacturing technology for subwavelength nanostructure coatings on this scale do not exist, though vacuum deposition processes are under development. While vacuum deposition processes for creating nanostructures are potentially scalable technologies, it is typically argued that "wet deposition only" based techniques are typically lower cost.

We have investigated proof-of-concept development for a two-step wet deposition process of a scalable nanostructured coating. Dielectric nanospheres monolayers are wet deposited to form a template followed by the wet deposition of much smaller metallic nanoparticles which form a mesh-like structure by filling the valleys formed by the hard-sphere packing of the template particles. Structures are then annealed to sinter the metal nanoparticles. This nanomesh geometry is chosen because it is known to have an optical resonance. This process could also be adapted to photonic structures through a different choice of materials for other applications. For example, photonic periodic hole mesh-like structures have identified application in high brightness LEDs for solid-state lighting and radiative cooling for buildings. More complex structures with other functionality, including sensing, could also be imagined once the basic process has been demonstrated.



Schematic representation of the two-stage deposition of the nanomesh film: (A) a dielectric monolayer nanoparticle template formed on the surface, followed by (B) deposition of the second, smaller metallic nanoparticles or nanoink; (C) scanning electron microscope results demonstrate a nanomesh metal film created under this project.

During the course of this project, we have been able to demonstrate small scale proof-of-concept nanomesh fabrication via the two-stage wet deposition described previously. Preliminary optical data on these films exhibit an optical resonance, which is very promising. We are currently working on a peer-reviewed publication to disseminate our findings.

To create the nanomesh films, we experimented with multiple sizes of nanoparticle template and nanoink materials to optimize this process. Results indicate that multiple size template particles are workable, depending on the desired optical properties. However, it was found that smaller nanoink particles tended to yield better results. The quality of the coatings was highly dependent on deposition speed, wetting and surface treatment of the substrate, and drying conditions. Numerous trials were conducted systematically to vary each of these conditions to determine the optimal results. Defect control is still an issue and includes holes and multilayer islands in the template material in addition to overfilling and partial "decoration" defects in the nanoink deposition. It is expected that most of these defects can be controlled and mitigated by using higher quality substrates and improved nanoparticle template monolayers.

In addition to experimental efforts, numerical modeling was performed to elucidate the predicted response of these types of nanomesh structures as a function of potential fabrication parameters. For this effort, appropriate nanostructure unit cells were created and used periodic boundary conditions. Finite difference time domain methods were then utilized to solve Maxwell's equations over a mesh defined on the structure. Results showed a tailorable resonance dependent on fabrication parameters.

PN15041/2716

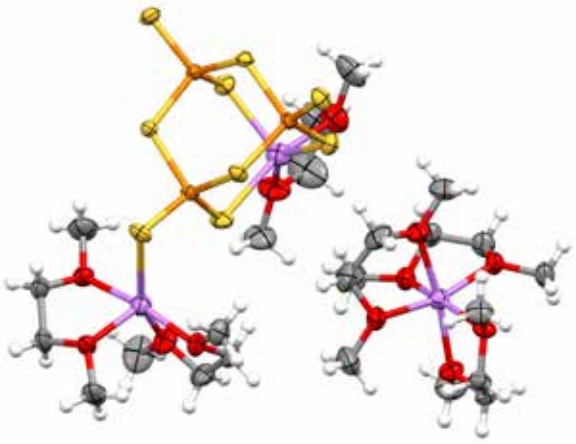
Tailored Electrolytes for Lithium-Polysulfide (Li/PS) Redox Flow Batteries

Wesley A. Henderson

Under this project, we developed new catholytes (e.g., electrolytes containing an active cathode material) capable of stabilizing diverse lithium sulfur (Li/S)-based active species in the liquid state for developmental Li/S redox flow batteries intended for electrical grid energy storage.

Li-ion batteries based upon graphite anodes and metal oxide insertion cathodes have achieved impressive energy densities. Unfortunately, such batteries do not meet the demanding cost-energy requirements for stationary (grid) energy storage. Tremendous attention has therefore been devoted to lithium-sulfur (Li/S) batteries (with Li metal anodes and solid carbon-sulfur cathodes) in recent years. Inexpensive earth abundant sulfur is electrochemically active with a high theoretical capacity indicating that Li-S batteries may have a theoretical energy density of 2600 Wh kg^{-1}. Intractable problems persist, however, with the development of such batteries. Unlike the insertion cathodes that are used extensively in current Li-ion technologies, sulfur undergoes a series of chemical/structural transformations during the battery reaction from insoluble elemental sulfur (cyclic S_8) to various lithium polysulfide (Li_2S_n) species to insoluble sulfides (Li_2S_2 and Li_2S). The longer lithium polysulfides tend to be soluble in the liquid electrolyte, resulting in instability to the solid cathode structure, difficulty in utilizing all of the active material (i.e., S), and poor cycle life (charge/discharge performance). These critical challenges have been difficult to overcome.

Recently, however, a Li-lithium polysulfide (Li/PS) battery was demonstrated in which the cathode active materials (lithium polysulfides) remain in solution (i.e., as a liquid catholyte instead of a solid cathode), thus avoiding many of the problems associated with the solid carbon-sulfur cathodes. Unfortunately, the energy density of this battery is limited (170 Wh kg^{-1} theoretical value) due to the cycling (limited voltage range) restrictions imposed to prevent the crystallization of insoluble solid phases (Li_2S, Li_2S_2 and Li_2S_4, as well as S_8). Dramatic increases in the energy density of Li/PS (or analogous Na/PS) batteries, which may be optimal for grid-level energy storage from the potential of operating these as hybrid redox flow batteries, will require catholytes that retain the lithium sulfur-based species in the liquid catholyte.



Ion and solvent coordination in the structure of the $(G1)_6$:$Li_3P_3S_9$ crystalline solvate (purple=Li, red=O, yellow=S, orange=P).

Motivated by the need, we explored the solution characteristics and electrochemistry of soluble sodium and lithium salts with polythionate and phosphorus sulfide anions. Initial work focused on preparing sodium polythionate species via the reaction of sulfur (S_8) with $Na_2S_2O_3$ (and other ionic salts) in a wide range of solvents. The solubility of the resulting salts proved to be low, except when dimethyl sulfoxide (DMSO) and tetramethylene sulfoxide (TMSO) were used, which resulted in dark purple solutions. Unfortunately, there are indications that this improved solubility is actually due to the reaction of the sulfoxide solvents with the polythionates.

Our work transitioned to phosphorus sulfides for which a diverse range of anions may be simply prepared by heating Li_2S (and S_8) with P_2S_5 in a solvent. Polyethers such as glymes (G1-monoglyme, G4-tetraglyme, etc.) were effective at dissolving 1/1 Li_2S/P_2S_5 compositions to produce concentrated catholyte solutions. Both Raman and ^{31}P spectroscopy characterization methods confirmed that the phosphorus sulfide anions were similar irrespective of which

Examples of G4-phosphorus sulfide catholytes with differing amounts of either $LiBF_4$ (left) or $LiCF_3SO_3$ (right).

PN15045/2720

glymes were used as the solvent. The addition of another lithium salt as a supporting electrolyte did in some cases strongly influence the phosphorus sulfide anions present. The solutions were yellow in color when either $LiCF_3SO_3$ or $LiN(SO_2CF_3)_2$ (LiTFSI) were added, but the solutions became clear and colorless with a small amount of precipitate formation when heated instead with $LiBF_4$. Extensive Raman and 31P spectroscopic evaluations indicated that this color change originates from a radical transformation of the phosphorus sulfide anions present. Solutions with G4 remained liquid, but a $(G1)_6$:$Li_3P_3S_9$ crystalline solvate formed in some of the solutions prepared with G1 and LiTFSI (note that this solvate does not contain the TFSI- anion), which suggests that the $P_3S_9^{3-}$ anion may be prevalent in solution. The electrochemical analysis of these catholyte solutions demonstrated that the species were electroactive within the range of 0.5–3.5 V (vs. Li/Li^+), indicating that a range of electrochemical reactions occur between these and related anions.

Ultra-Low Background Polymers for Structural Applications in Radiation Detectors

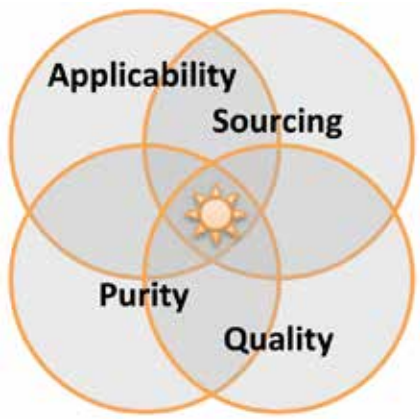
Jay W. Grate

This project focuses on the materials required for ultra-low background insulation (i.e., plastics) for next generation detectors in high energy physics programs.

Ultra-low background radiation measurements are essential to several large-scale physics investigations such as those involving neutrinoless double beta decay, dark matter detection, and solar neutrino detection. Ultra-low background counting is also of value in applied radiation detection applications associated with nuclear security and treaty verification. To detect low probability events, it is essential that the background noise of the measurement systems be driven to the lowest achievable levels. Hence, the radioactive contaminant species in the materials used to make and house radiation detectors must be minimized. Radioactive impurities in materials can arise from naturally occurring isotopes, radionuclides generated by cosmic ray interactions, and anthropogenic sources. The radioisotope purity required for these detectors goes well beyond even the best industry practices for chemical purity.

Considerable work has been done to purify germanium as the primary semiconducting detector material. Ultra-pure copper production for low background systems is well underway for structural parts requiring electrical or thermal conductivity. However, there remain needs for electrically and thermally insulating dielectric materials with extremely low background radioactivity. The materials must be especially low in uranium (U), thorium (Th), and potassium (K) and not be contaminated by radon daughter products. This project is focused on plastic polymers for use as structural materials. Specifically, thermoplastic polymers represent the class of dielectric materials capable of meeting the requirements for ultra-low backgrounds, mechanical rigidity, and suitability for forming or machining into detector parts. These materials cannot be evaluated or qualified for detector applications unless a method exists to assay the polymers for trace contamination. The development of assay methods is coupled with sourcing, evaluating, and improving plastic polymer materials.

We made great strides in sourcing and obtaining thermoplastic materials early in the supply chain to prevent grinding, pelletizing, thermoforming, handling, and transporting activities from contaminating and confounding our ability to understand the inherent purity of the plastic materials. Both nonfluorinated and fluorinated materials with excellent structural properties have been obtained in flake, powder, pellet, or 3D printed forms. We also made progress in assaying samples of these plastics for U and Th. In one approach, a solution containing the metals and radiounclides from the plastic is analyzed by inductively coupled plasma mass spectrometry (ICPMS). The challenges to this approach include breaking down the plastic and creating the solution, the absence of reference materials as laboratory control standards, and avoiding contaminating sample solutions with traces of metals from the container materials used in sample preparation. In another approach, we used laser ablation (LA) to sample polymer materials for ICPMS analysis, which reduces sample preparation issues. This new method is being developed to address fundamental challenges in using LA-ICPMS as a quantitative method.

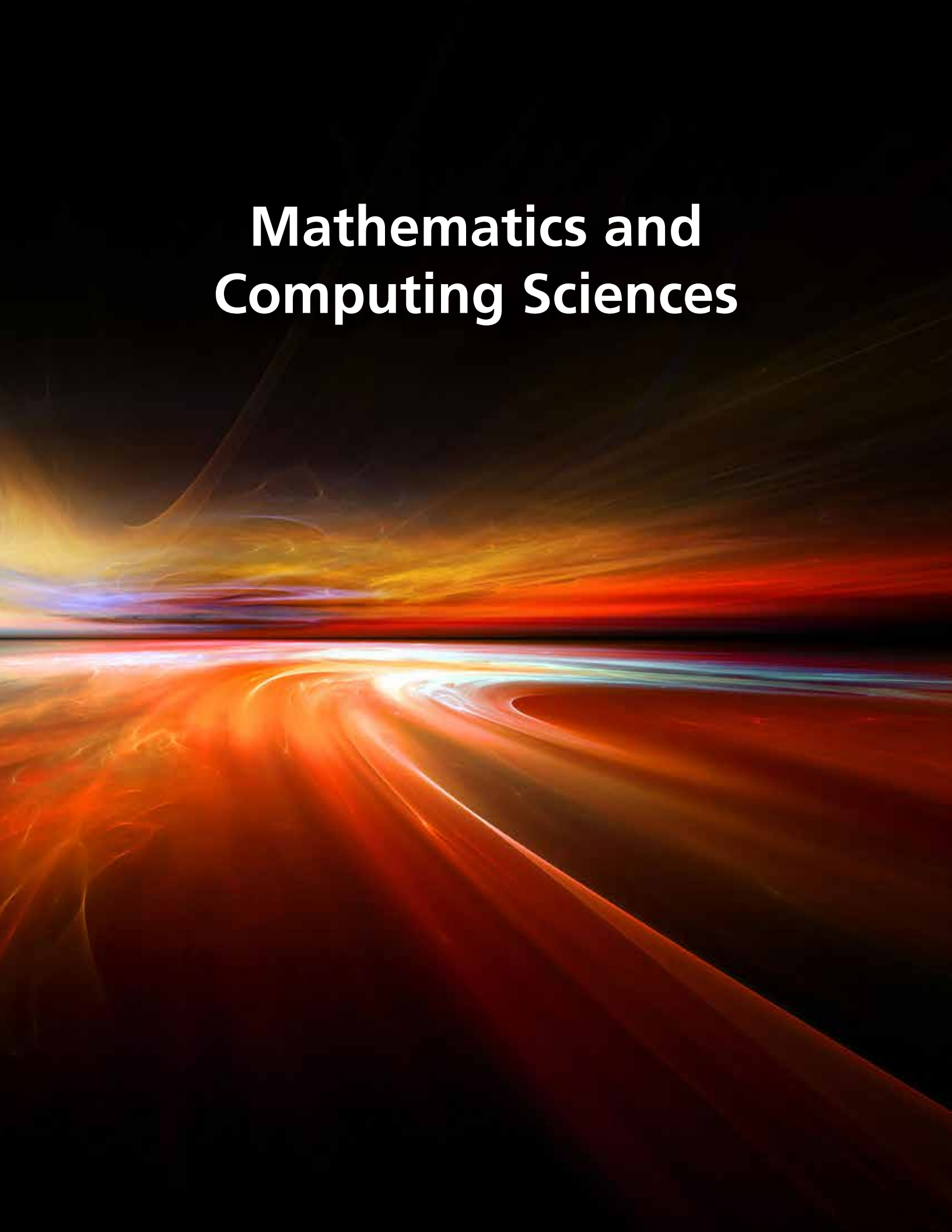


To create a sustainable capability in ultra-high purity plastics for detector applications, materials must have correct structural and insulating properties and be sourced at early stages from reliable manufacturers so that subsequent handling and part formation does not cause contamination. Additionally, materials and processes must be developed to provide extremely pure parts with quality assured throughout, requiring the development of new assays for contaminants in plastic materials at levels far below those of industrial practices for chemical purity.

We successfully sourced and analyzed fluorinated and non-fluorinated structural polymer materials with radiopurity levels in the low micro Bequerel (Bq)/kg range, orders of magnitude below the 10 to 10,000 milli Bq/kg of typical commercial thermoplastics. Indeed, one material we obtained assayed to single-digit micro Bq/kg, indicating very favorable inherent powder purity. We developed a new assay technique for determination of U and Th in solid plastics to levels in the single micro Bq/kg. The radiopure materials we assayed have been powder or pellet raw materials. Future work will focus on the radiopurity of solid materials and parts made from such raw materials.

PN14003/2587

Mathematics and Computing Sciences



A Population Based Approach for Hypothesis Generation and Control

Alejandro Heredia-Langner

Our work is developing a systematic approach for the construction of reliable classification systems that can function in high throughput environments and generate useful hypotheses for analysts.

Large, complex multivariate data streams are common in today's environment in which companies produce records with activity data from commercial entities and private individuals. Searching in an exhaustive manner for an optimal combination of classifiers suitable for application to a data stream is feasible only when the number of individual classifiers considered is small. Currently, other research efforts in this area focus on searching the space exhaustively or in some other computing-intensive way. When that approach is not feasible, random selection of a classifier is often recommended.

In our approach, the search for combinatorial space spanned by classifiers is performed systematically and iteratively, learning from previous results the measurement of how much testing is required to arrive at a classification system with good performance. This methodology is widely applicable, and it could prove particularly useful in high rate, large volume data environments in which reasonably rapid responses are needed. Our approach is based on the use of orthogonal arrays that have optimal statistical properties to determine the effect of each individual classifier on the performance of the ensemble and detecting interactions between individual classifiers that lead to significantly more accurate predictions. Creating effective, agile, and simple classification systems in the way we propose is crucial in high throughput environments to enable researchers to make sense of the overwhelming amount of information, and intervene only when necessary.

As an initial demonstration of our approach, we characterized the commercial behavior of a group of companies in a common line of business using a small ensemble of classifiers on a stream of data with over 50,000 records containing commercial activity information. Using a systematic testing plan, we found a subset of classifiers that can be used to predict company labels with reasonable accuracy. Performance of this classification ensemble, measured as its error rate under stable conditions, has been characterized using an exponentially weighted moving average (EWMA) statistic, which can be used to monitor the record stream with data from the commercial network to determine when significant changes have occurred. Our results indicate that larger classification ensembles are not necessarily optimal, pointing to the need to search the combinatorial classifier space in a systematic way. The results also show that current and past performance of a reliable classification ensemble can be used to detect when statistically significant changes in company network activity have occurred. The dataset we used contains high level commercial activity information, continuous and categorical variables, and involves hundreds of companies, making classification challenging.

In our work, all possible combinations of four different classifiers were tested. Our results show that the most complex classification system (in which all four classifiers are used) does not result in the highest accuracy or smallest variability. This leads to the question of how much effort is required to produce a classifier with optimal or near optimal performance in practice. Our results in this case, and a second where records from 30 companies in six different lines of business were analyzed, clearly indicate that optimal or near optimal classification performance is achievable with a relatively small classification system. This finding has practical consequences in applied areas because simpler, smaller classification systems are easier and computationally cheaper to train.

To simulate a type of change in the activity of the commercial network that would be of interest to a business analyst, labels for test records of two of the companies involved were swapped. This change, which simulates companies in the network behaving in an unusual way, impacted around 6% of the test records, leaving the vast majority of records in the test set unchanged. Using the EWMA statistic on the modified test records showed that our approach was able to detect quickly a significant degradation in classifier performance. These results are encouraging because they show that the classifier can maintain a level of performance as long as the data stream remains stable, and that an out-of-control signal occurs quickly when significant changes have occurred. In this way, the analyst is called to intervene only when the system has sufficient evidence that changes are needed. Results from this work have been published in the Proceedings of the 2015 International Conference on Data Mining.

During FY 2016, we will demonstrate more widely the applicability of this approach using a variety of benchmark datasets available. We will also apply the methodology to data streams of particular interest to PNNL, including imaging data from a transmission electron microscope and a stream of records containing chemical analysis data obtained using nuclear magnetic resonance, among others, placing special emphasis on incorporating user input. We envision that these results will lead to two or three more publications describing the methodology and the applications, and to a new way of measuring local classifier diversity that can be used by practitioners when designing and creating classification ensembles.

PN15021/2696

Analytic Framework: Signature Discovery Workbench

Nathan O. Hodas

The Signature Discovery Workbench (or Workspace) provides a visualization of information where signatures can be created, used, and adapted.

The Signature Discovery Workspace (Active Canvas) provides a facing application to allow users to create multimedia signatures quickly and efficiently for classifying information from disparate data sources across multiple domains. The system will allow rapid comparisons between new and existing signatures as they are being developed, enabling informed decisions about multimedia content through user interaction and features extracted.

Our approach was to leverage prior work in semantic interaction to formalize signatures based on user interactions. Our project aimed to answer the following research questions:

- How can we infer the process of signature discovery from information synthesis through user interaction of the information?
- What is the tradeoff between explicit signature creation (using the radial decision tree) and implicit signature creation (using the spatial canvas)?
- How do user-defined spatial visualizations impact the signature discovery process when the process/workflow itself is abstracted?

To address these questions and accommodate user feedback into the signature creation process, we developed a new spatialization visualization of domain-specific data to steer and augment signatures. Based on user research across the three domain areas (Bio, Nuke, and Cyber), spatialization visualizations are leveraged as visual metaphors to gain an overview of classification and clustering of information as well as a means for exploring relationships that form between the information.

As part of this work, we added new algorithms and models into the Laboratory Integration Framework and Toolset (LIFT) architecture to support this research. Lighthouse is a proven image and video processing system previously leveraged in the Canopy application. Specifically, Lighthouse extracts features from images and videos that can be used to describe the content and create relationships based on those features. We also incorporated text analytics from InSpire to bridge multimedia content effectively from text, image, and video.

The new spatialization visualization allowed us to infer analytical reasoning associated with specific interactions afforded in the visual metaphor, whereas workflows and signatures are implicitly created on behalf of the user. We shifted user focus from actively building a workflow to analyzing and synthesizing information spatially while the workflow is inferred and implicitly adapted. Next, we introduced "attractors" for information based on individual signatures. These seed the clusters of information and drive the meaning behind spatialization areas. Finally, we provided support for multiple data types, including images, text, video, and sequence data as sustained by a related project. The user focus on the synthesis of this information will align our research with crucial work through the data types selected and the analytic steering of signatures through the inferred reasoning of the user interaction.

In addition, we developed a method for capturing user interaction so that we could understand how that interaction affects the information theoretic feedback loop that will facilitate the signature discovery process. This scenario allows the "crowdsourcing" semantic feature extraction from which we will create stronger, more meaningful information classifiers. We also developed a closed loop for interactively training the system to place items where the user needs them. We plan to publish the research in conferences in our field.

Active Canvas enables users to create signatures derived from information clusters extracted from features and manual interaction by the analyst. Each cluster can be quickly converted to a classifier as a signature for the information presented.

PN13020/2501

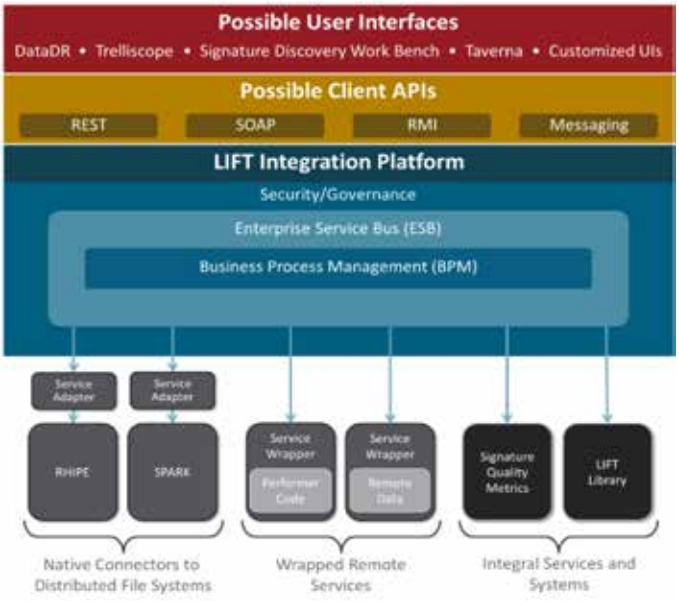
Analytics Integration and Validation Framework

Ryan R. LaMothe

The goal of this project is to enable the integration of multidisciplinary research efforts and their products into a unified framework for the discovery and validation of complex signatures.

Software tools and infrastructures for the discovery of domain-specific signatures are in use and well known. However, none has the flexibility and the reusable methodology required to be extended into multiple domains. Typically, these tools are applied *ad hoc* for the task at hand or they are integrated using workflow software, which provides a graphical interface to integrate disparate software tools. For either case, the methodology is not made explicit, in that it is tied only to a particular scientific domain or not documented systematically. This situation 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 maximize the high performance computing resources that are required to solve many of these problems.

Our research leverages multiple developed capabilities, including analytic framework architecture, signature quality metrics, and signature processing algorithms developed under multiple projects. To support the execution of commonly used signature discovery methods and algorithms, we created a flexible, lightweight integration platform that can incorporate existing and legacy tools into a single system known as the Laboratory Integration Framework and Toolset (LIFT), which adapts to client needs by allowing users to choose appropriate tools to address their particular signature development needs and deploy them to the environment of choice. These tools are made available via LIFT-supplied web services that are accessible from a wide range of client tools. LIFT achieves several core goals by reducing trial and error, allowing users to reuse existing tools and approaches, and providing a reproducible mechanism for constructing and evaluating signatures. This methodology encourages reusability and reinvestment, and is actively being used to develop signatures in a wide variety of domains.



LIFT architecture

This enterprise-quality integration platform exhibits the following features:

- Modularity – The integration framework allows analytic services to be added and removed readily.
- Deployability – The system can be easily deployed and fielded through the use of flexible profiles that abstract away host-specific information.
- Interoperability – Web services are used to make analytic tools available to a wide range of client tools and programming languages.

In FY 2015, the analytic framework team partnered with challenge project teams across the internal group to encapsulate algorithms and tools into LIFT web services available to other users. These collaborations resulted in the successful integration of capabilities and workflows from multiple projects, including Fishing for Features, MLSTONES, and PILGram. A LIFT Analytics-as-a-Service (AaaS) cloud-based prototype was developed and is planned to be merged with a codebase next year. At the same time, existing software was deployed to the PNNL Research Cloud.

The maturity of the system is exhibited by the fact that LIFT has been adopted as the integration framework for two PNNL divisions and external projects sponsored by DTRA, DHS, IAEA, and Special Programs. Additionally, PNNL LDRD leadership has recognized LIFT's cross-cutting value and is considering supporting the framework for all applicable future research initiatives.

In FY 2016, the team will continue to support signature challenge projects through LIFT's novel AaaS platform, which will also be an integral part of PNNL's Research Cloud efforts in coming years.

PN14015/2599

Applying the Active Data Canvas to Biological Sciences

Samuel H. Payne

This project opens a bold new vision for what collaborative science and data analysis should be. The Active Data Canvas promotes multi-disciplinary team science analysis and speeds scientific discovery.

As datasets increase in size and complexity, it is increasingly difficult for the end-user to access the data in a meaningful way. For biologists, ecologists, and clinicians, it is particularly difficult to apply domain expertise successfully to convert data tables into knowledge. Such challenges cannot be addressed with additional computers or even more computer scientists, yet domain experts must be able to explore their data. Paradoxically, this issue is not a computational gap, but Big Data has created a scientific community divided by the formal expertise that is required to perform facets of the discoveries undertaken. We contend that this problem is caused by a fundamental usability issue in which computational expertise is required to perform the data analysis and is often, unfortunately, capability that the scientists may not possess.

This research project is creating interactive data visualizations that are familiar to scientists and thereby promotes browsing. We will also research the most common data transformation steps and how these can be done on-the-fly so that domain experts can explore hypotheses productively. The overall goal is to create a tool that enables teams to analyze data productively and collaboratively; the tool should also proactively identify relevant results and/or resources that assist scientists in their analysis. The desired technical achievement is to create a tool that is visually appealing and instantly useful to broad domains of biology.

In brief, all research tasks for this project have been completed. The expression matrix functions properly and for large datasets, communicating effectively with the canvas. The pathway view works and communicates with the canvas. The canvas itself works but requires some additional effort to make completely robust, and the assistants creating recommender cards are also complete. The applied research tasks that focus on deployment are underway, and we anticipate finishing them within the next year. The GitHub connection is finished, and the creation of an external server is at the stage of various approvals.

The heatmap view is often the first place at which individuals begin to work. It provides both a familiar context and one in which people have a lot of curiosity. We have a working heatmap that does on-the-fly statistics for both differentiating experimental meta-data (columns) and also enriching genes/pathways (rows). These features have been well received as people viewed the demonstration. We have also worked with multiple datasets for the generality of function for the heatmap viewer. Another familiar format to the users are diagrams from Kyoto Encyclopedia of Genes and Genomes (KEGG), a database of biological system functions. The pathway viewer layers data onto the KEGG. Working with KEGG's database, the integration of our data on top of theirs has been relatively easy.

The Data Canvas view is a place to save data and explore ideas. When this feature has been shown to users, they have been impressed with the ability to bookmark data and have a proactive search of relevant literature and knowledge. The most important finding was that users loved the visualization. We did a user study on the tool, and the usability scores were extremely high, especially after users were asked to perform the data analysis manually. Visualization was seen as a dramatic improvement and consistently revealed aspects that users had not noticed when performing functions in manual mode.

PN15063/2738

Characterization of Anonymous Peer-to-Peer Networks

Curtis L. West

This project examines the content and technology behind the evolving social and technological movement surrounding anonymous peer-to-peer networks.

Anonymous peer-to-peer networks and related technology for the sharing of illicit materials and for non-attributable, encrypted communication are a worldwide movement that is growing in terms of impact and sophistication. FreeNet, GnuNet, Retroshare, Tor Hidden nodes, and I2P are all peer-to-peer networks that exist now and allow users to exchange data, chat, and blog anonymously. These networks are ideal for sharing illicit information, as they protect the identity of the source and recipient and also provide a distributed peer-to-peer cloud in which the content is stored. Radical decentralization appears to be an over-arching goal.

In this project, we are seeking to define rigorously the landscape of anonymous peer-to-peer (P2P) networks in terms of technology and content. Although there is a great deal of literature on various technologies that contribute to these networks' capabilities, there is little on the evolution of the technology, its actual (not assumed) content, scale, and general use patterns, and its emerging future. We are striving to achieve the following: 1) develop the capability to characterize and assess the ongoing use of these networks in both scale and topical space; 2) develop capability and expertise in these technologies and report on the landscape in terms of maturity and technical capabilitiea; and 3) suggest future directions for technical and policy related work.

We have observed a wide variety of technologies that appear to be converging in the areas listed below:

- crypto-currencies
- peer-to-peer technologies
- the idea of the "block-chain" as a contracting mechanism and general public ledger
- alternative network technologies and protocols
- encryption.

This "radical decentralization" movement is aimed at replacing common elements of our current culture with what we call social machines. Elements to be replaced include central banks, fiat currencies, internet service providers, voting mechanisms, domain name service, trade regulation, and other critical elements. Once designed and released, these social machines run independently from any given individual, group, or state. If a saying could represent such a movement, it would be the following: "There is no trusted third party; trust only the math."

While the specific goals of each network, technology, currency, and other elements are quite varied, the effect of anonymity tends to support the proliferation of a wide variety of illicit use. These networks provide the basis for a current and future worldwide criminal services ecosystem. Conversely, they also provide a mechanism for the oppressed to share information and communicate with some degree of privacy. Our research takes a valuable neutral approach.

PN14011/2595

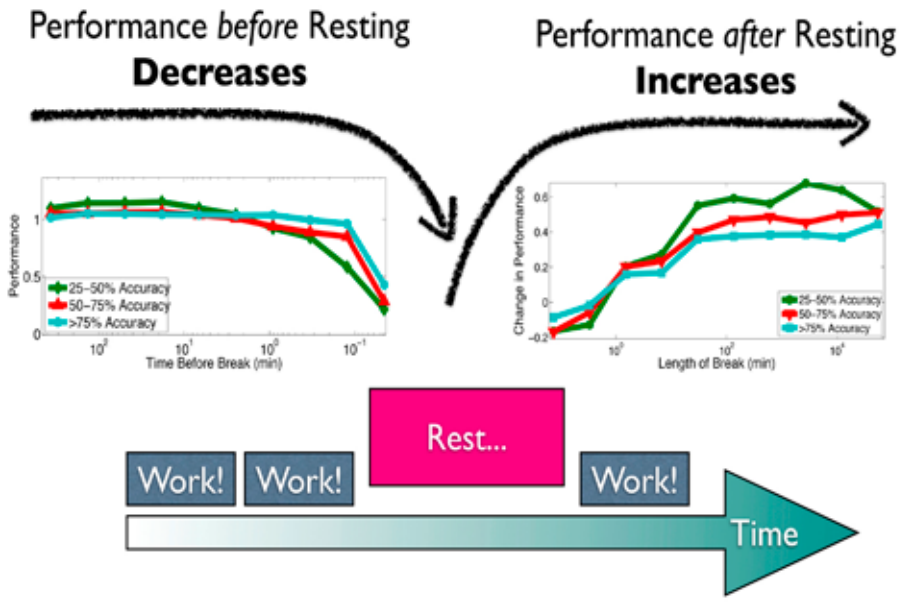
Cognitive Depletion in Streaming Environments

Nathan O. Hodas

In this project, we examine the attempts to leverage techniques for modeling cognitive resources to create adaptive systems that extend peak performance.

The problem of mental fatigue has been widely studied, but the results of past research have been highly contradictory. Although one's intuition is that mental fatigue can be offset by rest, the relationship between training, performance, and fatigue remains poorly uncharacterized. Many studies show only a weak relationship between self-assessed fatigue and actual cognitive performance; others have linked impulsive behavior (e.g., "ego depletion") to the loss of finite willpower and executive function. These latter works have been controversial, in part due to difficulty of replicating the work and also from the challenge of clearly measuring ego depletion. In short, there is no clear mechanism to model the processes proposed and no simple manner in which to design experiments or protocols to manage ego depletion and hampering progress.

We are using our domain expertise in cognitive energetic modeling, human-computer interaction, and controlled human experiments to provide unique, valuable capabilities to identify and mitigate cognitive depletion in intense streaming environments. We use these models to understand cognitive depletion and then predict the state of the user, enabling systems to weigh user actions and provide direct feedback to users, alerting them when performance decline is predicted. Using a combination of physiological models and machine learning, we make recommendations to users as to when they should take a break: before the effects of cognitive depletion start to degrade performance.



Anyone who has performed decision making over extended periods is familiar with the feeling of cognitive depletion: increased impulsiveness and errors, slower evaluation of new information, and decreased memory retention. We identified cognitive depletion among video game enthusiasts' activity, people taking standardized tests, and document rating.

In FY 2015, we explored cognitive depletion in a number of tasks, including standardized testing, video games, and document ratings. We identified that users tend to decide to take breaks when they become extremely depleted. Using these breaks as a guide, we were able to identify the signatures of cognitive depletion in all three settings. By comparing behavioral patterns with observed performance, we have concluded that cognitive depletion may be characterized as increased impulsiveness and errors, slower evaluation of new information, and decreased memory retention.

Additionally this year, we constructed a streaming system for predicting user performance in video games. The system provides feedback to the user regarding whether the user should continue on and play the next game. Our streaming system for evaluating cognitive depletion increases performance by avoiding periods of fatigue, and not simply waiting to identify the errors associated with fatigue. We also designed a user study to evaluate cognitive depletion in expert users of NMR spectral classification software. The experiment will be conducted at the end of FY 2015 or in early FY 2016. In addition, we are entering collaborations to continue tracking cognitive depletion in other projects, particularly science of interaction-related experiments.

By understanding the theoretical principles of cognitive depletion and measuring the condition in controlled situations, we will be able to design more effective systems to help users avoid cognitive depletion in real time. This understanding will also enable us to provide feedback to human-in-the-loop systems regarding the fatigue state of the user.

PN15022/2697

Compression Statistics for Analysis of Streaming Data

Jeremy Teuton

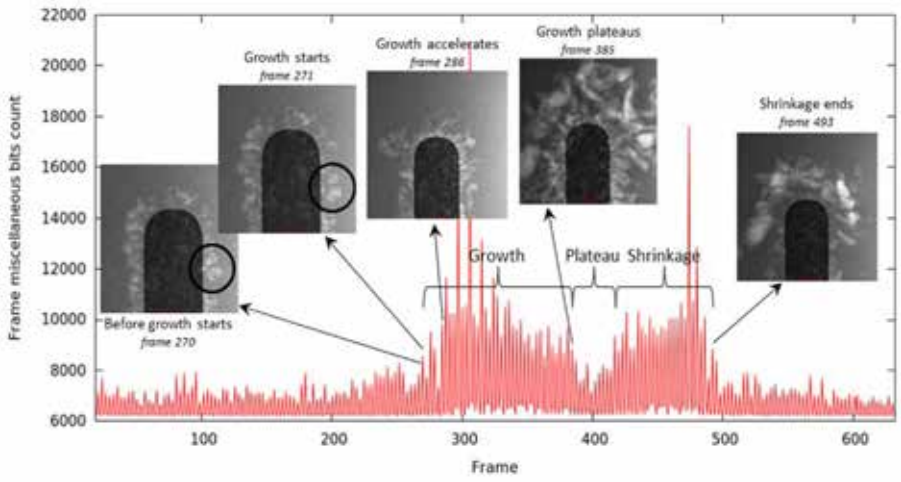
We are leveraging metadata generated by compression algorithms to detect and potentially classify events. The value is not in the compressed product but in the meta-data generated during compression for rapid analysis of streaming or very large data sets.

Efficient compression of video uses multiple calculations comparing current to previous to facilitate compression. In this work the value of these algorithms to speak to specific changes is to be leveraged both with native image/video data and with non-video data sources processed as video. Statistics on what percentage of an image moves, what fraction move in the same direction, contiguous shapes or isolated blocks novel vs shifted pixels etc… will be used in data in analysis to identify and potentially classify events in streaming data. This use of compression algorithms is a novel approach to enable analysis of streaming data, or to speed analysis of very large data sets in real or near real time, without having to write new customized algorithms for every new data set.

This work will provide the basis for a new flexible modular tool for streaming data analysis support. Gaining a solid understanding of current strengths and weaknesses of this type of analysis compared to the state of the art rule based video and streaming data analysis will define both its best use cases and areas for further research and improvement. In addition, the work offers a strong basis for further development of the toolset and identification or creation of optimal algorithms and should deliver a solid research tool to determine cost benefit tradeoffs in computational power and required training.

In FY 2015, compression analysis has validated and expanded the initial concept of using video compression software for analysis of data beyond the first use on electrical frequency data, demonstrating its capacity to work with multiple data types. These data sets included scene detection in normal video, event detection in nuclear magnetic resonance data, and automated analysis of electron microscopy experiments that detect the first moment of dendrite formation in a lithium ion battery (the event that eventually leads to failure of the battery).

Data quality can vary drastically by source and type; sensors are limited in quality and degrade due to time and conditions. To access our method's sensitivity to data quality, a video file with complex scene changes was analyzed at varying degrees of degradation from pristine to nearly unrecognizable by human eye. Despite being unwatchable with changes significant in exact value, the compression metadata did not change pattern, the method remained able to detect events despite the degradation. These results are critical as we move into use cases where for various reasons the data quality will be far less than ideal.



An example of how variations in video compression algorithm metadata accurately identify important events in an experiment. Still images called out by our analysis as important and categorized are connected to variations in metadata (a single piece of metadata "frame miscellaneous bits count") and used for clarity.

In FY 2016, we will expand to use and compare alternative video compression algorithms. The project will expand our analysis to support data from new partners and we will also expand into new use cases including conversion of single images into video format by subsection to roster through the image to automate crystallographic analysis. Our ability to ingest lower quality data will be exploited to integrate into compressive sensing techniques that allow much lower signal to be extrapolated into higher quality signals. Further the basic concept of exploiting complex compression and analysis algorithms to use for "off label" analysis will be tested in another project using text compression/analysis algorithms to analyze text documents, and data that can be represented in text format.

PN15011/2686

Co-Simulation Platform for Rapid Prototyping of Control Algorithms

Jeffrey A. Daily

This project is developing a unique tool/infrastructure that will position PNNL as a leader in modeling complex systems for evaluating controls for the interaction of power grids, buildings, transportation, and related domains.

The ongoing modernization of power grids consists of integrating with communication networks to achieve robust, resilient control of grid operations. The typical applications of this emerging smart grid, such as demand response, dynamic reconfiguration, and distributed energy resources employ control systems that operate on mission-critical devices. Beyond the smart grid, control systems are used in additional domains, including building management and transportation systems. As such, these applications of control systems need to be tested rigorously before deployment. Developers usually do not have access to a large test bed; therefore, simulators are used for testing control system applications.

There is a dearth of simulation software available for the intricate coordination and control of power grids, building management and automation, markets, and transportation infrastructure. Further, there are few (if any) tools for developing complex control algorithms within one or across two or more specialized domain simulators. Cooperative simulation of power grid, communication network, and building simulators coupled with advanced control algorithm implementations promises to reproduce more accurately the interactions of these components. Taken together, these domain components exhibit a macroscopic behavior not predictable by examining the individual entities. This is a complex system, and there is an immediate need for the control of such a system. Co-simulation is thus the most cost effective means of rapid prototyping and testing new control approaches.

The objective of this project is to deliver a general, scalable co-simulation platform for use in various domains. In addition to the direct support of power grid, communication network, building simulators, and advanced control algorithm implementations, our platform will support hardware-in-the-loop capabilities. We are thus striving to advance the state-of-the-art in co-simulation environments, focusing on the needs to support developing complex control algorithms across diverse simulator software packages and hardware.

The culmination of our FY 2015 efforts resulted in the release of our new co-simulation software framework, the Framework for Network Co-Simulation (FNCS) version 2.0. FNCS 2.0 features a new publish/subscribe messaging paradigm that greatly simplifies the experimental setup of a co-simulation. Data streams can be abstractly represented and fulfilled by a simple playback of data, a sophisticated simulator software package, or a hardware signal. The entire system is extensible, connecting arbitrary data sources and sinks. These data streams are fully synchronized by the FNCS 2.0 broker application and can be represented at different time scales, as needed.

A large number of simulation software packages have been modified to use FNCS 2.0. These simulators include MATLAB and, by extension, its many packages: MATPOWER; power distribution simulator GridLAB-D™; network communication simulator ns-3; and whole building energy simulator EnergyPlus. In addition, FNCS 2.0 is fully cross-platform capable, running on Windows, OSX, or Linux systems, or any combination thereof. As a result, we are now well positioned to target the integration of any simulator software on any operating system platform.

Integration with the experiment management system and other projects is well underway. This procedure highlights our success integrating FNCS 2.0 and its related simulators into our envisioned test bed. Though each project can stand on its own, the whole is greater than the sum of its parts. We successfully showcased an integrated demonstration to our internal annual review committee, receiving high marks and praise to continue with our endeavors in earnest.

In FY 2016, we will implement the first hardware-in-the-loop use case, in addition to developing larger-scale use cases in preparation for FY 2017. Supporting hardware-in-the-loop was part of the FNCS 2.0 design since its inception. To that end, we began investigating the incorporation of OPAL-RT in FY 2015. Specifically, we added the Python and C programming language interfaces to aid in the integration. We have always targeted large-scale simulation; however, we have only run on the order of tens of simulators to date. In FY 2015, we also performed some basic scalability tests that will help us improve our implementation for FY 2016. In addition, we began to develop comprehensive models that will depend on FNCS's capabilities to run large numbers of simulators.

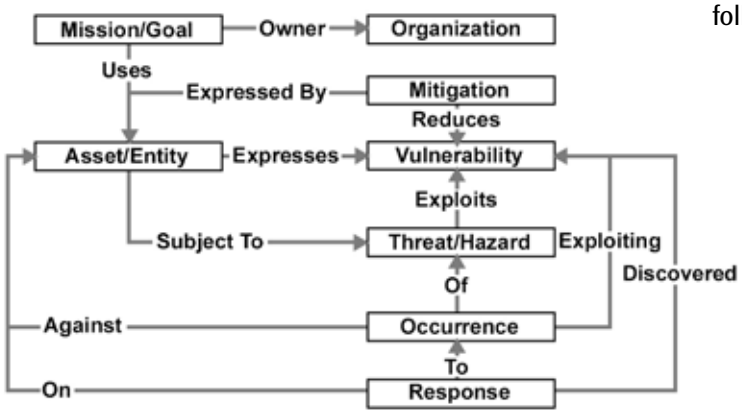
PN15009/2684

Cyber Risk Assessment Model (Cyber RAM)

Michael A. Corsello

This project focuses specifically on deepening the understanding of how an organization relies upon its cyber infrastructure to accomplish critical missions.

Cyber security is an area of current concern and an immense opportunity for attackers. Any and all mechanisms that can convert the favor of the defenders, especially against poorly defined attack vectors or insider threats, are of particular significance. This research is focused on two primary "soft" aspects of security: involvement/engagement and inter-organizational communication. The project specifically creates a technology model to capture and convey the inter-organizational dependencies on technology within an enterprise (information technology [IT] infrastructure mapping onto non-IT operational missions) and between enterprises/departments (sales department reliance on inventory management department), with a mapping of the missions to the underlying infrastructure providing the mission capabilities. The current status and completeness of the data will be ensured by facilitating the integration of data capture to "hands-on" operators of the missions and infrastructure rather than relying on subject matter experts (SMEs) or IT staff to capture this information. This approach of distributed data capture is a variation on the theme of "crowdsourcing" to augment SMEs and instrumentation data that will be relevant in applications well beyond the cyber security domain.



Model of risk-related entities and relationships between those entities influencing risk

The development of an approach to analytics over a distributed graph will provide significant improvement in the ability to scale cyber network and system topology-based (and any graph-based system) analytics in the operational setting without the need to resort to exotic technology and approaches. The Cyber RAM approach provides a distributed model which has direct implications to the efficiency and effectiveness of cyber security throughout the attack lifecycle by focusing the attention of defenders to areas of greatest weakness to infrastructure supporting operational missions rather than to operational infrastructure itself. This approach acts as a force multiplier by providing a means of more effectively "moving the bottleneck" away from the most critical missions to mitigate impacts before and during attacks.

Cyber RAM will provide a specific implementation of a general concept that will scale and integrate with other infrastructures and hazard types to provide a foundation for enterprise-wide risk management across all infrastructures for all failure/hazard modes, including multi-modal hazards (cascading hazards). While the current project does not focus on this area, the technology implementation is directly transferrable to the broader infrastructure picture.

Over the limited course of evaluation this year, the Cyber RAM project saw an alignment with operational need and found no directly competing projects or products. There has been limited overlap with other products that captures a skeleton of information around assets and missions, but none provides an analytic capability. There is potential for other follow-on work that might build upon this research effort.

PN14088/2672

Cyber Security Testbed and Dataset Generation

Thomas W. Edgar

We are designing and implementing a common infrastructure shared by cyber security researchers with the aim of accelerating research and development, advancing the state of cyber security science, and eliminating the expense of operating redundant experimental platforms.

Cyber security suffers from a lack of scientific rigor that slows advancements made in the domain. Specifically, the science of cyber security is immature and often lacks necessary conditions of repeatability and reproducibility, attributes that inform scientific quality. A common research infrastructure like the one created by this project—including an experimental platform, reasonably realistic models and simulation, tools to control experimentation, and the stewardship of datasets—shared by like investigators will advance the state of the science, accelerate research and development, and reduce costs associated with redundancies.

In FY 2013, our efforts were aimed at understanding the ways in which testbeds can be built and instrumented so that they provide a valuable platform on which to conduct experimentation. Desiring enterprise scale, we determined that virtualization was a must; thus, we investigated several different virtual machine monitors (VMMs), a hardware/software system for creating, executing, and managing virtual machines. Using the capabilities of virtualization to create an instance of a small business network, we generated synthetic datasets using a PNNL-developed cyber-user behavior modeling framework and made these sets freely available to researchers. Last year, we organized our efforts into three categories: standing up CyberNET, an enterprise computing experimental testbed; modeling and simulating; and gathering and stewarding datasets. In CyberNET, we consolidated the resources under OpenStack cloud computing platform. These changes provided central management of the resources and an abstraction that permits researchers to easily instantiate models.

For FY 2015, we achieved three overarching tasks: integrating a user modeling framework, developing testbed capabilities and modules to stand up a fictional company, and expanding and testing the cloud platform underlying the testbed for science. For modeling and simulating, we evaluated cyber-user behavior modeling frameworks, designed and instantiated a network instance of a reference architecture, and designed a framework for modeling cyber-social behaviors. We evaluated the cyber-user framework that was used in the year prior, specifically noting that the behaviors generated were often incomplete and demonstrated artifacts. One example was a temporal correlation of what should be independent behaviors. Additionally, the framework suffered from resource constraints and would halt unexpectedly. This challenge added complexities to generating datasets, as only after inspection of the resultant datasets could we detect defects. Due to these problems, we began collaborating with MIT LL on the Lariat tool to provide the user simulation capability needed. We subsequently began expanding the tool to provide the functionality and models needed to stand up our fictional reference company.

Our project designed a network model in FY 2014 that fulfilled the requirements specified in the reference architecture. We used a three-tier hierarchical internetworking model as a guiding principal, incorporating fault-tolerant/redundant components at multiple OSI levels within the design. The model was then stood up within CyberNET. During FY 2015, we moved beyond the network model to the business model of our testbed and defined models of departments for HR, software development, and sales, each including the necessary services and user roles in each. We then configured the necessary software and simulation framework to mimic the fictional company. Several projects actively used the project to test assumptions and demonstrate proofs-of-concept.

Finally, in our review of existing cyber-user behavior modeling frameworks, we observed that the frameworks ignored cyber-social interactions, activities within which an enterprise exist with email, web, and user applications. One way to model user behavior realistically is to analyze social interactions (first order and higher) among users. The approach began with simple, automated agents and added complexity as required to be consistent with observed data. Our primary data source for deriving and validating our approach was a set of connection records for emails and phone calls obtained from the PNNL enterprise. Our data-driven, agent-based

PN13051/2532

modeling approach was infused with models of social interactions between agents, producing a prototype tool that demonstrated realistic email social behaviors.

We approached datasets differently than in the previous year, whereby we moved away from generating synthetic datasets to gathering and stewarding real, semi-synthetic datasets. We archived PNNL enterprise operational data (upon approval) as well as several exercise datasets. Additionally, we hosted a capture-the-flag exercise and recorded the resultant data. We also began data curation, which included organizing a metadata catalog that explains the types of data within each set and defines sufficient safeguard mechanisms to anonymize and sanitize data.

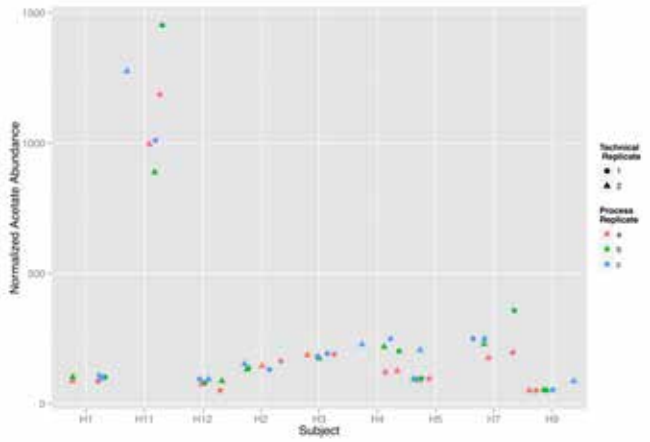
Finally for FY 2015, we wanted to complete our process of creating a scientific tool out of a cloud platform. To accomplish this effort, we studied the behavior of the testbed under different network and load conditions to see if it behaved consistently. In some cases, it did not; to remedy this situation, we developed additional capabilities to control network behavior, sensor network communication, and auto-document the experimental environment. All of these capabilities helped the users of the testbed create and perform more rigorous experiments.

Developing Signatures that Relate Fecal Microbiome Characteristics with Gastric Bypass Surgery Outcomes

Nancy G. Isern

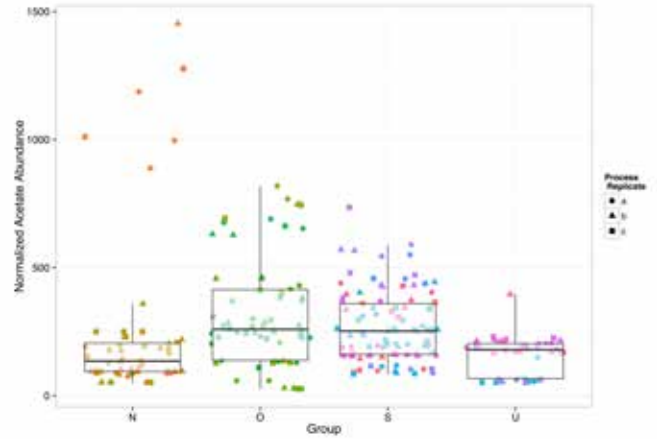
The methods developed in this project will help us understand the biology of fecal microbial communities in relation to human hosts. These data interrogation tools will be applicable to such diverse areas as biofuel and bioproduct production.

In collaboration with Arizona State University (ASU) and the Mayo Clinic, we are exploring fecal microbiome biomarker relationships using a combination of disparate data types for anticipating patient responses to gastric bypass surgery. Our broad goal is to advance microbiome condition understanding as it relates to energy regulation and patient responses to the most commonly performed bariatric surgery in the United States, the Roux-en-Y (RYGB) gastric bypass. We are exploring the relationship between the patient fecal microbiomes and gastric bypass health outcomes, searching for biomarkers or clusters thereof that relate to the composition of the fecal microbiome and patient health status. We completed initial data analysis of metabolomics, microbial taxonomy, and patient metadata using PNNL's Tessera Tools and are presently commencing additional data collection to develop composite bio-signatures that will allow us to discriminate patient groups, providing predictive indicators of surgical success while offering insight into host-microbiome metabolic interrelationships.



Subject variability of acetate abundance for the lean control group

Our effort differs from related research in three fundamental ways. First, we are using novel tools and statistical methods developed recently that have not been used previously in metabolomics studies. Second, we are leveraging five different



Group variability of acetate abundance

data types, where previous studies have used only a subset. Finally, we possess robust datasets with at least 10 biological replicates per subject group and have recently expanded our retrospective study to include new patient samples that will allow a prospective arm of the study, with samples derived from both pre- and post-surgical patients. We believe that our project represents a unique opportunity to apply these contemporary methodologies to a rich, combined dataset consisting of multiple data types, thus facilitating predictive systems biology not only for our immediate application but also for other systems biology research.

To date, nuclear magnetic resonance (NMR) metabolomics data, 16S RNA sequencing taxonomic data, and patient metadata have been combined using datadr and were subsequently visualized in Trelliscope, providing a quick and easy assessment of data outliers, allowing us to re-examine the data analysis, correct errors, and assess variability among biological, process, and technical replicates. We also used a naïve classifier to search feature space and identify variables across the data types that most reliably discriminate patient groups.

We are presently beginning additional data collection on matched sample aliquots for both the retrospective and pro-

PN14083/2667

spective arms of the study. NMR spectra are currently being acquired, and methods are being finalized for liquid chromatography (LC)–mass spectrometry (MS) fecal bile acids analysis and gas chromatography (GC)–MS-based fecal metabolomics. In total, we will have over 80 matched samples for data analysis. Once we have the datasets, we will move into full-scale analysis, integrating five specific, discrete data types: NMR 1D and 2D metabolomics; GC–MS metabolomics; LC–MS bile acids determinations; parent grant 16S rDNA sequencing data; and parent grant patient metadata. We are in the process of exploring various normalization strategies for the NMR and 16S data.

Trelliscope has been used to create user interface (UI) visualizations to allow for data to be explored interactively to search for relationships and patterns between the patient fecal microbiomes and gastric bypass health outcomes. Fishing for Features and a Bayesian Integrated Feature Finder will be used to identify the analyte sets that can be used to classify each patient optimally into one of the four known patient groups. Statistical cross-validation and Signature Quality Metrics will then be used to assess and compare the various combinations of features and classifiers (i.e., candidate signature systems) used to construct an optimal model for predicting obesity in RYGB patients and controls.

Development of an Computational Image Analysis Tool

Richard E. Jacob

This project is designed to develop a novel, image texture-based analysis tool that is fast, automated, objective, non-invasive, and based on widely available imaging technology.

Subtle variations in the texture of 3D images can be key to discriminating materials or detecting early changes. The human eye is not well adapted to detecting subtle variations in image texture or grey-scale intensity over a wide area; therefore, sensitivity and specificity for detecting subtle patterns is highly operator dependent. To this end, research in computer-aided detection (CAD) has typically targeted the identification and characterization of key image features. However, the detection and characterization of image texture changes may provide additional information about subtle yet important characteristics ranging in applications from concealed explosives to lung disease. CAD is necessary to advance routine image analysis beyond the physiological bounds imposed by the human eye.

This project focuses on the application of the variogram, an established geostatistical image analysis tool that visually represents spatial heterogeneity or roughness to 3D images that have subtle textural anomalies. Our primary objective is to develop a fully automated, rapid, and robust approach to CAD in 3D images to allow for the assessment of subtle textural abnormalities that might be detected by the human eye but more likely would be missed altogether. The ultimate goal is creating a software tool that can be deployed for a routine application in a variety of contexts. We therefore focused on human lung CT images because they display predictable yet subtle changes in texture with disease progression and because we have access to hundreds of well-characterized images to test our tools.

A key issue in developing variograms for universal application is that there is a wide range of parameters that affect image quality and noise, even at the same site using the same equipment. Noise is a key issue because it directly affects image quality and can mask the textural variations that this method is designed to detect. A key accomplishment of this project is that we developed a novel method for noise correction in variograms using voxel blocks of various sizes taken from different regions of the image. These voxel blocks are used to reduce the effective image size and computation time by factors of hundreds or thousands. For example, a region of an image with an empty background containing only noise can serve as a baseline for the rest of the image. If this region is relatively small such as the trachea of a lung, it requires smaller voxel blocks to obtain statistically significant results. However, these smaller blocks will give varying results, as different variograms give diverse results, depending on the size of the voxel block used. Our method is to apply different sized voxel blocks to the varying regions of the lung and then use extrapolation to develop a correction factor based on the noise background. This activity has never been done before in variograms or 3D imaging.

We adapted our existing variogram code, which was originally written in Python, to C. The outcome is a more universal software platform that performs much more efficiently, resulting in a reduction in the computational effort of approximately 100 times. This feature will help strongly facilitate eventual commercialization and deployment. The new code also resamples the images to isotropic resolution without the loss of information.

We demonstrated that the variograms of human lungs suffer from mischaracterization if the tracheas are included in the computation. This issue is a key problem to solve so that all variograms are applied consistently across patients, imaging platforms, and sites. We began to develop a method to detect and segment the trachea automatically to eliminate it from the calculations. This activity proved to be an exceptionally challenging problem, as normal image-to-image variations in quality and size are confounding factors. Nevertheless, our method was successful in approximately 80% of the images we tested. However, to make it more robust, some additional work on the algorithms of trachea recognition is needed.

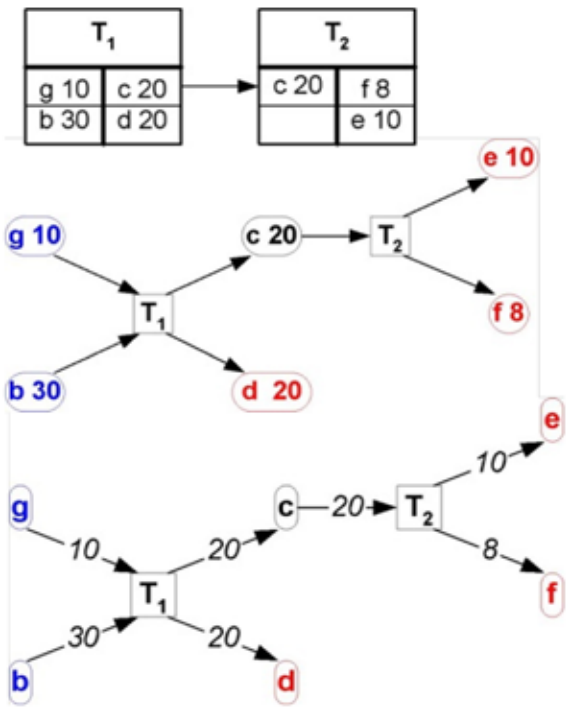
PN15057/2732

Digital Currency Graph Forensics to Detect Proliferation Finance Patterns

Sean J. Kreyling

We will provide methodologies for identifying patterns of illicit activity derived from large anonymous data networks and establish PNNL's leadership in modeling global-scale, decentralized ledger systems.

Financial systems have matured with Information Technology (IT), first through the digitization of banking and credit networks (together with central banks) and more recently through the rise of digital currencies and cryptocurrencies (CCs), the most prominent of which is Bitcoin. The attraction of digital currencies to criminals, in particular the ability to launder or transfer funds for purposes such as the trafficking of nuclear materials, poses severe technical challenges to both technologists and analysts. In particular, the ability to identify patterns of criminal behavior in the publicly available information derived from large anonymous data networks requires novel technological developments around graph data management, pattern mining, and modeling. Through this project, we are examining the open and publically available historical data for CCs transactions (e.g., the Bitcoin blockchain) and attempting to identify patterns of illicit activity.



A sample transaction in Bitcoin represented as hypergraph edges.

In FY 2015, the team began developing fundamental engineering capabilities for placing the publicly available historical information (i.e., blockchain) in a relational database (RDB). We designed an RDB schema for Bitcoin and verified its sufficiency and compatibility with the hypergraph mathematical model. We began to parse the compressed transaction data, which is challenging due to binary coding and other software engineering issues. Additionally, we identified existing academic research on the network and its most basic properties, including some pre-parsed network data.

Specifically, the team initiated a process to identify relevant available financial datasets, including both traditional (bank or credit card networks) and CCs. Special focus was placed on the blockchain and associated graphs of CCs, through which we became familiar with the state-of-the-art analysis for financial forensics and started building formal graph models of financial networks, including CCs and linked CC traditional networks. We conducted research into various money laundering and money transfer methods and developed a semi-formal conceptual and/or process models for each. We also initiated a review of the literature on anomaly detection in financial data and created a plan to conduct exploratory data analysis on the historical blockchain dataset. Finally, we identified money laundering and transfer typologies associated with nonproliferation financing and conducted a review of the potential "red flags" for proliferation threat financing and money laundering.

Through an open literature search, we established that detecting money laundering in conventional payment systems generally relies on known identities and does not require a full picture of all transactions. However, we hypothesize that this approach will not be as effective in a CC payment system (e.g., Bitcoin), which must rely on an imperfect knowledge of identities but may leverage near-perfect knowledge of all transactions in the network because all transactions are publically available for all time. We believe that this insight will be important when assessing possible options for detecting money laundering or money transfer in the blockchain dataset.

In FY 2016, we will be working on two tasks. First, we will work on graph pattern identification, finalizing and then translating our money laundering and money transfer conceptual models into formal graph patterns applicable to CC blockchain graphs. Within this effort, we will develop graph-based pattern matching algorithms to be deployed on graph databases and assess various graph analysis tools for suitability. Second, our scaling focus will expand the above approach from a single CC to multiple-component financial networks. Finally, we will deploy the appropriate graph analysis tool for the appropriate scaling to giga-scale financial data.

PN15017/2692

Discovery of Cyber/Physical Qualifiers' Relationship and Relevance to Probabilities of Detection/Non-detection Mitigations

John R. Burnette

We are developing probability metrics for detecting and identifying disruptive, destructive blended cyber attack tactics, techniques, and procedures for cyber and physical systems.

Critical infrastructure risk assessment approaches have evolved over the decades to assess specific organizational disciplines in an independent manner. Specifically, both physical and cyber security have robust programs to look at risk to a facility, but both focus on their discipline and not at the risk of an adaptive adversary with capabilities in both areas. Further, these security risk assessments are organized and regulated in an equally stove-piped manner, compounding the ability to develop an integrated approach to risk management that utilizes physical security, cybersecurity and cyber physical security. Integrated cyber-physical attacks are seen with increased frequency, and methodologies are needed to assess risk and identify the relationships, touch points, linkages, and qualifiers necessary to mitigate blended threats against U.S. critical infrastructure.

This effort seeks to simulate the cyber physical environment to capture the corresponding data that enable insight into probability detection as well as any interconnections between parameters in this environment that may arm defenders with sufficient knowledge to mitigate future attacks. These interconnections could be as simple as lapsed time or a correlation model between physical and cyber events or behavior. The data obtained from the blended cyber-physical use cases will be analyzed to identify the qualifiers for integrated threats and cross domain touch points and linkages for both cyber and physical systems.

Our work in FY 2015 identified the statistical research design for the project; developed the cyber-physical sequence of events for the RAVEN cyber test range; identified the data sources (agnostic equipment and cyber-attack methods for testing the cyber/physical hypothesis); and identified the type of attacker with a "medium" level of sophistication. We looked at patterns in the Closed Circuit Television (CCTV) time series analysis that correspond to ground truth events. Additionally, other known/ground truth events such as proximity access with a fake proximity card were not detected. In all cases, the early stages of this study indicate that patterns can be used as signatures to indicate malicious activity, while more extreme measures may be needed to detect other malicious events.

We also performed experiments related to unauthorized computer shutdowns. Preliminary results identify a simple pattern that can be seen in the time element, whereby an unauthorized computer shutdown can be noted quickly. The elapsed time in seconds of the activity of the administrative computer for each run clearly showed that the computer was shut down and re-started. Given that these particular computers are closely maintained, the unscheduled shutdowns should raise a flag for the system administrator. This factor, corroborated with the time of day and subsequent logon with an account, are definite indicators of abnormal activity.

In another experiment, a "rubber ducky" USB was used to simulate loading malicious commands and scripts to shut down the Industrial Control System (ICS) Human Machine Interface (HMI) by turning off all ICS components. Additionally, the rubber ducky issued a shutdown command to disable the air-gapped ICS further. The ICS HMI Event Logs did not provide information that indicated use of a USB device, such as a rubber ducky. However, a "power off" command could be seen in the ICS event logs that could alert defenders that the HMI was shut down and re-started. However, the abrupt stoppage of time continuity was a good indicator of abnormal activity, as ICSes are never shut down without prior knowledge, as they control critical assets that must be operational. A defender could use software-based Intrusion Detection Software (IDS) tools to monitor for unexpected shutdowns, re-starts, and logons, especially during non-working hours.

For FY 2016, we will be testing for both the overall time delay and overall system response, adding complexity to the cyber-physical sequence of events, and attempting to identify the probability metrics for both cyber and physical systems.

PN15096/2771

Dorci - The Defenders Role in Resilient Cyber Security

Daniel M. Best

Through Dorci, we are building a foundation of understanding the needs and roles of next generation cyber network defenders who use resilient infrastructures for a more secure network.

Current research has explored defender roles and responsibilities; however, it has been conducted without the introduction of resilient infrastructures. A foundation of understanding roles, responsibilities, and needs of cyber network defenders can be leveraged by new and existing research in resilient infrastructures to increase utility to defenders, minimize complexity, and assist with the adoption of the new technologies. The object of this work is to advance knowledge about enabling defenders to manage resilient cyber infrastructures without increasing their cost (resources) to do so. As architectures, algorithms, and methods are developed to make networks resilient to attack, the network becomes more complex for the defender to manage. If resilient cyber security research is to tip the asymmetric advantage, it must not increase the burden on the defenders who are understanding and managing the network.

In FY 2014, we started by evaluating the importance of a "current state" study in order to provide a context for future work. Preliminary questions to assist with the correlation between previous research completed were leveraged. Initially, we had planned on a scenario-based semi-structured interview to help users to imagine their environment. Next, we explored use of a table top excursive within which users would be given roles and responsibilities, activities will occur, and various options for actions taken. We determined that our study should explore resilient infrastructures but needs to be believable and reasonable to defenders today. While the implementation and adoption of resilient infrastructures is not widespread (and making technologies difficult to map), we had widespread support from other projects to help ground our research in the plausible domain.

During FY 2015, we concentrated primarily on developing a traditional technology study; however, much of the research will transfer over to resilient technologies, which we will be investigating in FY 2016. Key accomplishments for FY 2015 include the tasks described below.

Design development of human subjects study and game play framework. We built out the study to immerse participants into a cyber security scenario, leveraging the ViSR company profile. The game play mechanics, cards, and mechanism for following decisions will all transfer to the next year when looking at resilient technologies.

Creation of a study tracker application. To track the study during participation, we developed a Java application to track all participants' investments and actions, along with rolled probabilities of success by both the red and blue teams.

Additional studies. We conducted two industry, one research, and one government study, along with several pilot studies in order to refine game play as well as study effectiveness. All studies were well received and generated results for traditional technologies with interesting findings. All participants enjoyed the style of the study, and several requested that we returned to play the same game with other participant sets from the respective organizations.

Hosted a visiting researcher. We brought in a researcher from Middlesex University to assist our team with research questions regarding next year's resiliency work. With this collaboration, we were able to establish much of the groundwork necessary to build out our planned experiment with resilient technologies.

In addition to the above activities, we are working on two different papers for submission to an international conference on human-computer interaction.

PN14087/2671

Estimation of Battery State of Health Using Utility and Literature Data

Vilayanur V. Viswanathan

This project allows the estimation of battery state of health to enable individuals to use large-scale batteries reliably.

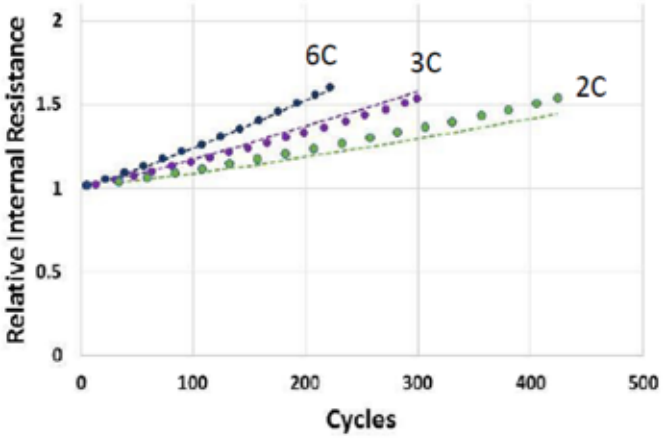
Understanding the degradation of a battery energy storage system is key to its deployability in stationary and transportation applications. Although the transition from consumer to large scale batteries is commencing in the automotive industry, questions about reliability and life still persist. Previous work in this area includes several model types, including empirical and fundamental physics-based, electrochemistry, and equivalent circuit-based as well as actual capacity loss measurements. In fact, the National Renewable Energy Laboratory (NREL) has developed an empirical model based on curve fitting to tease out dependence of capacity loss on time and number of cycles in the form of coefficients of time^0.5 (a1), time (a 2,t), and cycles N (a 2,N). However, these choices involved an empirical constant with little justification in the determination of the constant value.

In this project, we developed a model to estimate the remaining energy capacity of a lithium (Li)-ion battery cell or system through an algorithm that estimates resistance increase and capacity loss for the Li-ion chemistry.While the NREL work measured remaining capacity separately, our work directly estimates the remaining capacity from the estimated internal resistance increase based on universal curves that relate capacity loss to relative internal resistance increase. Specifically, our model continuously updates the status of a Li-ion battery state of health.

To begin the project, data from the literature were analyzed to account for battery loss during storage at various temperatures, cycling with various upper voltage limits, and cycling at various depths of discharge. The data were fitted to an equation with a t^1/2 and t term. For data that had different cycles per day, an elegant method was developed to determine the component with respect to t and component with respect to N. The dependence of these coefficients on temperature, upper voltage limits, and depth of discharge were obtained. Where data was not sufficient, simple assumptions were used.

In addition, we developed a way to determine estimated increase in internal resistance throughout the operation of the battery. Past work provided a way to accomplish the same feat, but at the end of a particular regime of operation, either storage at fixed temperature or cycling at various depths of discharges. We created a way to update the rates of degradation as operating conditions change to allow the estimation of internal resistance increase with time. In addition, we found that $LiFePO_4$ does not have a huge dependence on depth of discharge when it comes to its life and can tolerate high C rates of cycling with little effect on life.

In FY 2016, we will validate the developed model by applying it to the literature data. We already have the data in place and plan to get obtain additional data from Southern California Edison (SCE) and other utility partners, including small cell and system data, as available. Considering the promising progress obtained on our work to date, SCE is interested in continued collaboration, and this one-of-a-kind model work will be used with other projects, as there has been a need expressed for such a model in the industry.



C rate	a0	a1	a2,t	a2,N
2	1.020444	-0.02377	0.004325	-0.0029
3	1.016911	-0.0136	0.004325	-0.0029
6	1.015375	-0.01136	0.004325	-0.0029

The determination of the coefficient of time and cycles is based on data for a different number of cycles per day.

PN15101/2776

Exploring Multilevel Numerical Methods in Continuous and Discrete Systems for Extreme-scale Computing

Zhijie (Jay) Xu

This project is developing multilevel numerical methods for continuous and discrete systems that will significantly reduce the computational burden associated with uncertainty quantification (UQ) and facilitate the scientific discovery through efficient parameter estimation and data assimilation.

Many scientific applications involve equation systems that exhibit high nonlinearity and describe coupled physical processes across multiple time and space scales. The rigorous predictive models with UQ propagation capability require significantly more computational efforts in contrast to the deterministic simulations. This situation is especially true for climate modeling, in which a large number of ensemble simulations with multiple models or different parameterizations have been employed as an effective approach to quantify uncertainties associated with various processes in the model. Progress has been made on the uncertainty quantification for existing climate models such as CAM5 the Community Atmosphere Model (CAM5) using a large number of direct simulations (~200) and various sampling techniques for only 9 to 16 uncertain parameters. However, the view of exascale UQ as simply nothing but thousands of large-scale deterministic simulations can be misleading, as the most straightforward UQ strategy via generating many ensemble simulations to explore high dimensional space will not be feasible for the fast increasing number of uncertain parameters, even with the exascale computing power. This challenge calls for the urgent need of new numerical strategy in the context of extreme scale science. On the other hand, climate modeling inevitably involves data-intensive computing with ultra-scale and complex data generated from both models and observational programs with increasingly finer spatial resolution, higher frequency diagnostics, and more sophistication of physics (variables) adding into the models. How to use large volumes of observational data most effectively to improve the fidelity of predictions via efficient data assimilation is another challenge on the new numerical strategy.

Hierarchical multilevel algorithms can be applied to discrete systems, especially large-scale complex networks that appear in many applications critical to DOE's missions. The complex behavior of networks emerges from irregular topological structures and the interplay between structure and dynamics. Many network problems can be studied from the optimization perspective. One example is the state estimation of power grid systems, which can be formulated as weighted least squares. Challenges in this context include optimization and control of large-scale nonlinear systems that scale well on emerging extreme-scale architectures. Traditional Newton's method involves an inner-outer iterative procedure, often computationally infeasible especially for large-scale nonlinear systems. In the second part of this research, we will address these issues by designing novel methods for solving large nonlinear systems with the potential to reduce computational cost and save time by orders of magnitude.

To address the above challenges, we are developing hierarchical multilevel numerical methods for stochastic continuous and discrete systems that will significantly reduce the computational burden associated with uncertainty propagation, parameter estimation, and data assimilation. In FY 2015, we developed a novel, efficient UQ algorithm for exascale and data-intensive computing that can be applied to complex models, with the uncertainty entering through time and/or space correlated stochastic property field and initial and/or boundary conditions. The new hierarchical model presents two distinct characteristics: separation of uncertainty contributions from two different levels and from initial and/or boundary conditions and the random physical property. We will demonstrate that these characteristics offer immediate benefits to the computational efficiency.

We established a rigorous procedure to integrate parameter estimation and data assimilation for improved model prediction. Our preliminary results include advection-diffusion equation with observational concentration data corrupted by a given instrument noise. With our new method, we can estimate the unknown velocity field accurately from observational data. We are also demonstrating improved accuracy of short- and long-term probabilistic predictions

PN15070/2745

of concentration via rigorous data assimilation. Results indicate that the uncertainty in prediction can be incrementally reduced by the new method with an increasing volume of valid observational data.

We designed and implemented a multilevel method in time domain, often referred to as "parareal" method, hybridized with spectral deferred corrections (SDC) to solve a class of semi-explicit differential-algebraic equations (DAEs) for power grid analysis and optimization. Other applications of this type of DAEs include circuit and system design, robotics, and neural networks. This hybrid method aims at improving the efficiency and accuracy of power system dynamic simulations and is particularly suitable for running on massively parallel computer systems. The SDC method combines a Picard integral formulation of the correction equation and spectral integration rules to achieve stable method with arbitrary order of accuracy. The idea of parareal method is to break the global problem of time evolution into a series of independent evolution problems on smaller time intervals. By combining a prediction-correction approach with time discretization at multiple levels, the hybrid method converges fast with many available processors, eventually leading to the real-time solution procedures. We tested the hybrid parareal and SDC method on linear and nonlinear problems, and the numerical results are very promising.

The optimal control of power systems and other nonlinear systems often leads to nonlinear differential equations. After discretizing these differential systems, we obtained algebraic polynomial systems. Numerical algebraic geometry gives guidance to finding multiple solutions of the discretized polynomial systems (i.e., homotopy continuation and bootstrapping methods). However, these approaches are computationally intensive and can handle only polynomial systems of a small size. To combat this issue, we developed a novel reduced basis homotopy continuation method for computing multiple solutions of nonlinear system of equations. The efficiency of the proposed method is demonstrated through various numerical examples. This work has been summarized in a journal article to be submitted by FY 2015 end, and we are preparing three other manuscripts based on our work from throughout the year.

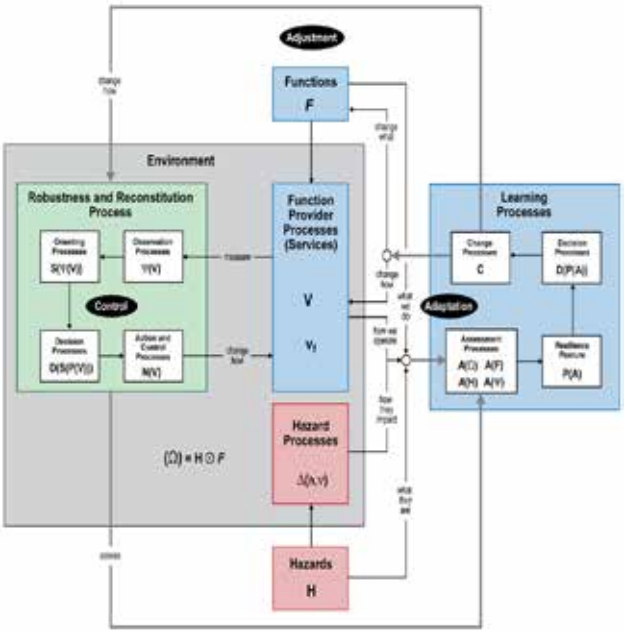
For FY 2016, we will continue applying our new method to the more general and complicated 2D and 3D parameter estimations and data assimilations that will provide more insight and test the method's validity.

Family of Resilience Metrics for Cyber Security Operations

Mary J. Lancaster

The development of operational resilience metrics will enable informed, objective cyber security decisions, cost-benefit analyses, and the development of both system resilience requirements and automated approaches to optimize system resilience.

Defining metrics for resilience in cyber systems has gained a considerable amount of recent attention. MITRE enumerates some 272 cyber resiliency metrics, including a subset that would be selected by an organization for use in a resilience assessment process. Some research provides a qualitative cyber-resilience assessment process, while others offer a hierarchical value modeling methodology for quantifying the resilience index in critical infrastructure. Although these metrics have been proposed, none has been widely adopted or made operational. An objective, reliable, repeatable basis for evaluating cybersecurity resilience is required: it facilitates discussion and decision making among stakeholders and cybersecurity practitioners, allows comparisons between system configurations, and enables the creation of minimum acceptable performance thresholds.



Cybersecurity resilience framework

The resilience framework outlined in this project enables strategic, tactical approaches to enterprise resilience and facilitates discussion among stakeholders and cybersecurity practitioners regarding the necessary features and measures of enterprise resilience. It fills a gap in the literature between high-level process management and low-level control systems. The development of a resilience taxonomy also fosters a healthy discussion about and creates harmonization of terminology. We propose the term "resilience posture" to describe the relatively persistent state of an entire IT enterprise system, a high-level quantifiable system attribute consistent with policy and management decision cycles. The degree to which the enterprise is configured to be resilient considers its intended purpose, known hazard environment, future assessment, and values.

The evaluation of cybersecurity enterprise resilience requires two types of measurements. First, the system must monitor various operational conditions critical to identify and respond to disruptions and enable a robust system. These measurements are part of one or more observation, orientation, decision, and action (OODA) loops that are a spectrum of autonomy from fully automated to human supervised. The second type of measurements include how well the OODA processes cover the critical enterprise functions and hazards to which the enterprise is exposed. The measurements allow an assessment about how well enterprise management processes anticipate, mitigate, and adapt to a changing environment. The assessment, decision, and change processes loop exists outside of this OODA control loop.

During FY 2014, we developed a theoretical framework in the form of definitions, a model, and a syntax to provide a mechanism for bridging resilience management process models (e.g., CERT-RMM) and the many enumerations of cyber-defense metrics that have been proposed (MITRE, CIS). We also developed an initial list of measures of resilience from the literature and subject matter expert elicitation. A test plan and procedures to implement the measures within the cybersecurity testbed have also been completed.

In FY 2015, we continued refinement of the theoretical framework, worked with the testbed team to develop the cybersecurity testbed, implemented measures in the testbed, and collaborated on the continued revision of the terms of reference. We proposed a three-pronged approach for the evaluation of resilience measures and metrics: descriptive case study, low-resolution descriptive modeling and simulation, and high resolution implementation in the testbed. We were only able to implement a single measure in the testbed due to environment limitations. It is expected that additional development will occur in FY 2016.

Our work was successfully submitted to an international systems engineering symposium occurring in 2016. As of the end of FY 2015, a manuscript describing a part of the project will be submitted for publication to a professional journal.

PN14009/2593

Fishing for Features: Discovering Signatures When the Underlying Phenomenon is Poorly Understood

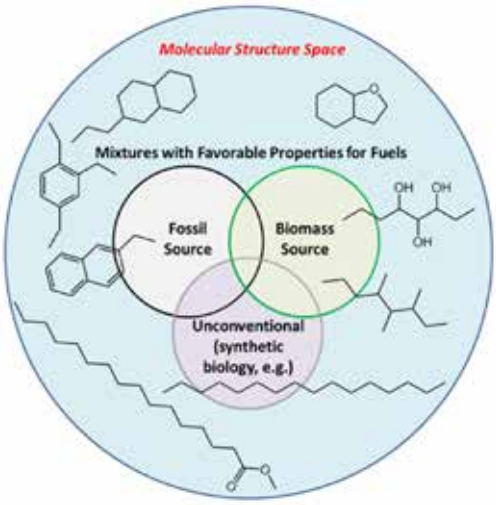
Kristin H. Jarman

We are uncovering methods for finding and validating signature features for high dimensional, poorly understood phenomena that can be applied to practical areas of interest. This work is relevant to high throughput and big data applications.

We live in an age of big data that touches virtually every aspect of our lives. Scientists can quickly collect terabytes of information on everything from a single atom to a complex living organism. Search engines and social media contain volumes of individual personal data. Online databases contain scientific information, consumer preferences, business performance, economic indicators, and more. As data availability increases, researchers continue looking for ways to use this information to gain insights into increasingly complex phenomena. In this project, we are developing signatures when the underlying physical or conceptual model is weak or not completely understood while working with datasets that are too large to search exhaustively and too complex for traditional optimization methods.

During FY 2014, we focused our efforts on two tasks. First, we optimized an individual re-identification modeling process using biometric features in which we developed a method to re-create a biometric signature for an individual using only the features available in a probe dataset. Our second task was searching and developing spectroscopic and chromatographic signatures to help predict important properties of bio-fuels and unconventional fuels, an area of interest to government agencies and private sector companies. In both projects, we employed a genetic algorithm (GA) to explore a vast problem spaces and created objective functions that helped the algorithm find reliable and informative solutions.

For FY 2015, we developed an approach to discover signatures of environmental perturbation in large biological datasets. The focus of our research was analysis of soil sample data obtained using Fourier transform ion cyclotron mass spectrometry (FTICR-MS), a high resolution MS technique able to resolve isotope masses with high accuracy, making it particularly useful for the study of complex mixtures. The main question of interest was whether features obtained through FTICR-MS could be found that discriminate between six experimental groups: two groups of soil cores transplanted between different mountain locations; two groups transplanted *in situ*; and two classes of soil not affected by transplants, referred to as native soils. Features that differentiate these groups can be investigated to determine whether they can be related to the changes introduced by the experiment. Discriminating features could potentially serve as a basis for creating a signature of the effect of dramatic climate change on this soil.



Fossil, renewable, and unconventional fuels and oils may be comprised of thousands of molecules, and some important characteristics of these fuels and oils are related to the molecular sub-structures of their components.

Principal component analysis (PCA) was applied to the set of available log-transformed FTICR-MS intensities. Of particular interest was determining if plots involving the first two principal components could provide visual evidence of the effect of the experiment on soil samples. A plot of component scores involving the first two principal components using all available features showed no discernible pattern in the distribution of points. Though the PCA did not detect association with the experiment effects, the analysis may be improved with the careful selection of features to detect signatures of the perturbation introduced among a large set of potentially uninformative variables. Feature down-selection with PCA can be performed in a variety of ways, and it is always challenging to find an optimal subset of features among very large sets of data.

In our approach, features were chosen using classification trees because of their ability to partition complex spaces in easy to interpret ways, their ability to work with binary features (using presence/absence of FTICR-MS features in this

PN13030/2511

work), and because they tend to perform well even in large problem spaces. We applied the classification trees to the FTICR-MS features in a recursive manner. In every iteration, features selected by the tree were removed, and the algorithm applied again to the remaining data. This procedure was used until a threshold of performance was reached. Application of this procedure to the soil FTICR-MS dataset resulted in a much more informative set of features when using component scores of the first two principle components. Our analysis revealed that the features selected separated soil samples first by where they had originated, indicating that any signatures relating to environmental perturbation need to be sought in samples with the same origin. Subsequent application of this feature selection methodology to soil samples with the same origin produced relatively small sets of features under investigation for biological links to changes introduced by the experiment.

A second application of the feature selection methodology was made on data from the transcriptomic analysis of a total of 59 individual cells in an experiment with four experimental treatments and a control group. Expression level data for 9233 genes was used to find signatures that can help distinguish cells exposed to different perturbations, and also to study the variability in groups of cells exposed to the same perturbation.

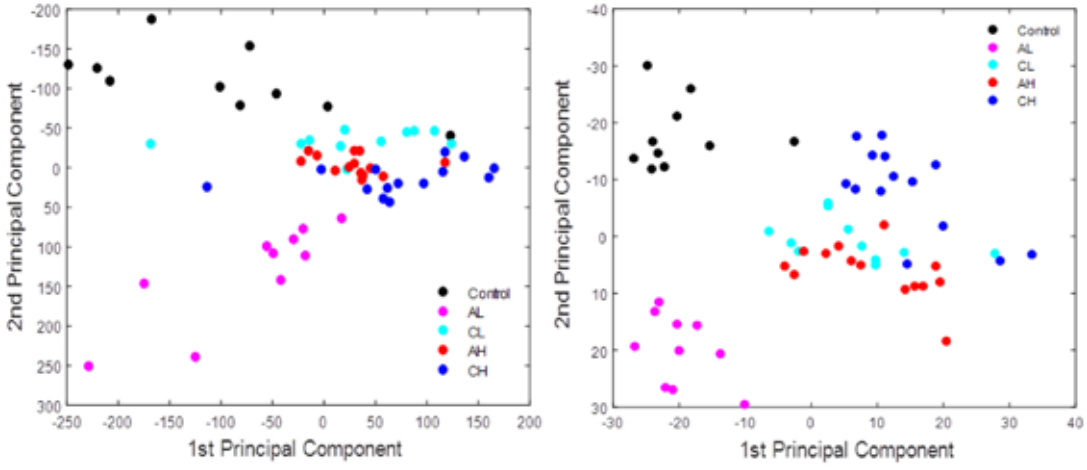
Results using PCA show that a group of 100 selected genes can distinguish cells by treatment groups better than the entire gene set. Analysis of two of the four treatment groups revealed one or two of cells within that group behaving differently from the rest, suggesting that there is a limited but significant heterogeneity among cells within a treatment group. PCA was performed using data from all cells, plus the normalized set of measurements from all 9233 genes. Visual inspection of the component scores plot involving the first two PC revealed that cells exposed to the NPs behave differently from the control group. Results also suggest that there are differences in how cells respond to different concentrations of the same NP.

The feature selection methodology described earlier was applied to the gene expression data, using the five different experimental groups as labels. The first 100 genes selected by this methodology produced better separation, when a component scores plot involving the first two PC was used, than that observed using all data.

Analysis of the 100 genes selected showed strong enrichment for functionality relating to cell cycle and cell stress. Because these genes generally show a (somewhat) unique expression pattern for each treatment condition, these results suggest that each experimental condition produces a distinct degree of stress in response to the treatment. While the process of selecting these genes allowed us to identify discriminating genes effectively, it also provided useful insight into the differentially affected processes involved in the various responses to the nanoparticle treatments. Further analysis of cells in each individual treatment group was carried out to determine the level of heterogeneity of cells exposed to the same perturbation. This is important because differences in behavior under the same experimental conditions can reveal clues as to the unique mechanisms cells use to respond to environmental insult.

Cluster analysis revealed that one cell in the control group and two cells in one of the groups exposed to low levels of the animated NP behaved differently from the rest of the cells in the same group. A search was conducted for individual genes that maximized the observed difference. The process produced a list of 200 genes for each of the divergent cells in each group targeted for analysis. The methodology applied in this work produces results that are obscured by traditional bulk-based experiments, and may be able to reveal important components of biological responses to environmental perturbation.

For the last year of the project, we will expand the use of our approach to datasets with new features and new biomass and research diesel fuels. The features will include high-resolution spectroscopic data like 2D-NMR, GC×GC, and FTICR-MS. We will iteratively select features, quantify performance of our methodology, and evaluate the applicability of our models. This process will allow us to establish strengths and weaknesses of our models and modeling approach, producing a better understanding of how spectroscopic features are related to the favorable properties we seek.



Plots using the first two principal components for the normalized gene expression of 9233 genes (left) and 100 selected genes (right) for the five different experimental conditions indicated in each plot.

PN13030/2511

High-Level Modeling Specification for Simulation of Control Systems

Thomas W. Edgar

We are accelerating the ability for control researchers to define and execute models of complex systems using simulation, emulation, and testbed tools by creating a coherent high-level modeling specification that abstracts the differences between technologies and domains.

A key aspect of effective tool design is to understand what is required for the user to be successful. In many areas of design and engineering, such an understanding is captured in a pattern language that captures good design practices. While features are broadly used to teach design skills and communicate successful design, we capture pattern languages directly into tools, frameworks, and literally in high-level specification languages in computer science. When appropriately designed, these specification languages guide their users to successful solutions as well as lead tool designers to features that reduce the cost and improve the reliability of designs even when made by comparatively novice users.

The name assigned to this project, Arion is a library of objects and capabilities built from the Java programming language to support the specification of complex systems of interacting components. The primary use case is to enable the modeling of complex systems with control mechanisms while abstracting the different technologies and methods the simulation and experimentation tools use to execute the model. In the development of new control mechanisms for complex systems, it is common to use simulators or emulators to run experiments to evaluate control mechanism behavior. While there is a range of strategies, Arion focuses on the scenarios in which the following situations occur:

- A system is described as a collection of components in which each component has internal state, consumes input signals, and produces output signals.
- Once elaborated, a system may be simulated to determine how the state of the system evolves over time.
- Each component is implemented by an execution host, typically a discrete event simulator or possibly a hardware emulator or hardware embodiment.
- The situation assumes that a coordination framework of some sort exists, which mediates the global notion of time and implements inter-host communication.

We are anticipating the need to generate hundreds of thousands to millions of components to form a system with multiple experiments that vary the structure of the system. Today, such experiments are often run by using a programming environment such as MATLAB or Python to generate input configurations for discrete simulators. Arion will subsume this step in the workflow and provide more cohesive integration that eliminates the necessary expertise in all of the configuration and specification language of each simulator or emulator.

An Arion script is a program that elaborates system components, their communication interconnections, the set of execution hosts, and the mapping of a component to a host. After this elaboration, the implementation of Arion generates suitable configuration information for each execution host, coordination framework, and computing infrastructure. We refer to this step in the workflow as compilation, to distinguish from simulation. Components may be specified as external components (those coming from the existing tool libraries) or Arion components (those components defined directly in the Arion language).

For our work on this project in FY 2014, the Arion team took the initial steps in developing this library of objects and functionality. Our first year goals were accomplished: the basic domain-specific language concepts were developed, and a prototype tool was created. Use cases, including a representation of the AEP gridSMART® Real-Time Pricing Demonstration project, were identified, and basic components and methodologies were extracted. GridLAB-D™ library components were added to the language to bootstrap using prior experience and extending this to the new test bed.

For FY 2015, the GridLAB-D™ library of components was made more complete, and components for ns-3 were developed and added to the library to support CDMA (Ethernet like) and WiFi connections. Also, the ability to compile configurations for the FNCS 2 co-simulation platform was made possible, and infrastructure definitions for the Experimental Management System were created. In addition, the preliminary capability to compile SQL database schemas from user defined variables to save was created. Leveraging all of these new capabilities, a complex model replicating the AEP gridSMART® project was created and successfully tested.

The plan for FY 2016 is to complete the GridLAB-D™ and ns-3 component libraries, extend the component library to include Energy+, Opal-RT, and Hardware-in-the-loop testing with the VOLTTRON™ platform, and to start a developing a library of common models of interest for quick-start research.

PN14046/2630

Image Analysis using Active Learning on Shape and Texture Features

Elizabeth R. Jurrus

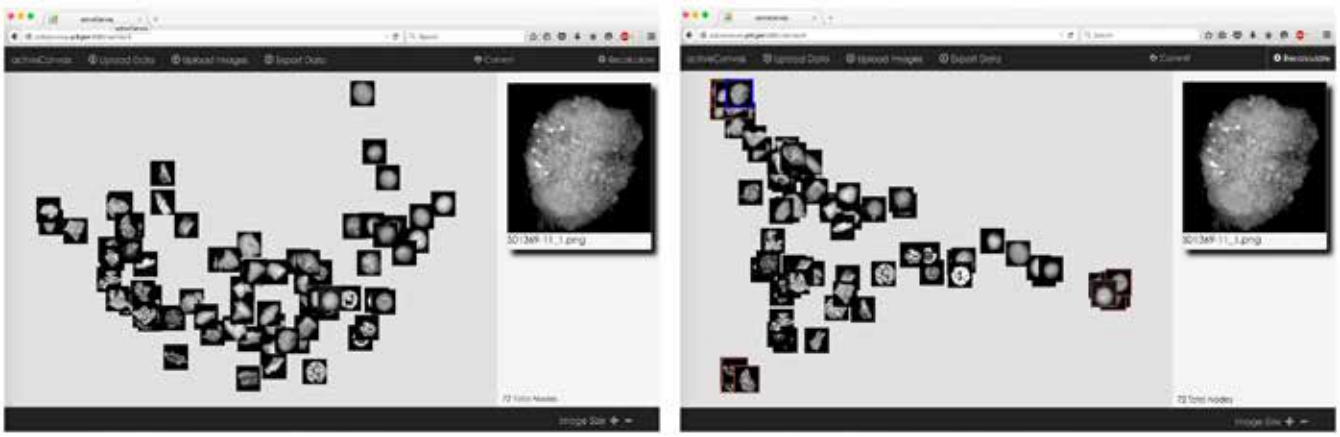
This project is producing an improved method for categorizing images from a data source given a small set of example images. Our new interface offers a method for scientists to access results of scientific experiments rapidly and correlate hypotheses with outcomes.

Automatic classification of large image datasets is challenging. As scientists develop improved image acquisition methods to capture data at higher rates, the amount of work required analyzing these images increases dramatically. Developing techniques using computer vision to address this issue can be difficult due to the complexity involved in choosing image features, having a lack of training data available for effective machine learning methods, and the lack of suitable user interfaces to parse through images. This research demonstrates a new method for categorizing images from a variety of data sources given a small set of example images or user input.

We leveraged two PNNL projects that use improved image feature extraction methods and machine learning with a "human in the loop" to present image data to users for fast organization. This approach provides scientists with an initial image data organization intended to show image variability in a 2D projection. Users interact with the images through grouping of similar images to improve the organizational layout; these groups become input to an algorithm that uses the feature vectors associated with each image to find similar images and projects associations to a 2D layout. This process decreases the time necessary to sort through large sets of image data.

Our active learning system, the Active Canvas, is built into a web-based application that allows remote hosting of images and facilitates user manipulation of image arrangements. Through this research, the interface has evolved to enable users to move and arrange images seamlessly, zoom, inspect, and color-code image group clusters. The resulting server-side services provide an engine for automated image layout based on the interactive user repositioning of images. In addition, users can add new images to the interface to aid in batch processing of incoming data. To represent the features for our images in our Active Canvas engine accurately, we incorporated state-of-the-art feature detectors from convolutional neural networks (CNNs) trained to classify natural images. Compared to other feature detector methods, we found that the CNN features provided the best qualitative layout for our images when projected to 2D.

We implemented an algorithm that leverages user interaction to improve the spatial data representation. As users interact with the image layout to move similar images closer together, our method adaptively updates user-created clusters either to include information about images moved closer to them or to eliminate information about images moved away from the clusters. Combined with the Active Canvas and our CNN feature vectors, this iterative approach efficiently enables users to organize image data.



Left: CDC nanoparticle images organized in the Active Canvas initial layout; right: tightly grouped by type, nanoparticle data after user interaction.

PN15064/2739

We applied our framework to two application areas to evaluate the usability and effectiveness of two methods. First, we examined a collection of nanoparticle images from a Centers for Disease Control and Prevention project and the PNNL geochemistry group. This work is investigating the amount of depleted uranium contained within an air sample to evaluate inhalation toxicity. Example screenshots from a user's perspective for this dataset appear in the images. In the second application area, researchers are interested in evaluating the effects of environmental toxicity exposure on the zebrafish. Fish exposed to different toxins develop different malformations, the quantification of which, along with identifying the toxin type, is a goal of this framework.

We found that interacting with image data through this interface provided a quick method for organizing image data and redistribution based on user-defined clusters efficiently moving images into meaningful groups.

Integrated Adaptive Resilient Asymmetric Data Security

Jian Yin

Our approach in this project significantly shifts advantage toward cyber defenders, making it possible to protect against zero-day security exploits.

Data confidentiality becomes increasingly important as more valuable and sensitive data are used by many essential online web services. It is desirable to build the capability to achieve resilient data confidentiality and integrity, in addition to availability in distributed environments. This capability should allow us to counter a wide range of security threats, including zero-day attacks and insider threats. One of the distinguishing requirements is resilience; that is, we can prevent the leaking of sensitive data or subverting integrity even when hackers compromise parts of the systems. Traditional approaches for cyber security are, however, mostly reactive and labor intensive. Cyber defenders must intensively monitor and analyze systems using various tools to detect and counter attacks. Once an attacker breaks into a system, at least some aspects of availability, confidentiality, and integrity are compromised.

In this project, our approach is that we can continue to provide data availability and integrity for mission critical applications and protect confidentiality of highly sensitive data even when attackers manage to break into or hijack part of system. Even though there are recent commercial systems designed to achieve resilient availability in the face of machine crashes or network partitions in distributed environments (including cloud computing), none of those systems addresses resilience against malicious attacks. If successful, the technologies and mechanisms developed in our project can be highly useful for our DOE and DoD sponsors, who have highly sensitive data and mission critical applications to protect.

In FY 2015, we developed algorithms with associated secure proofs, allowing us to establish a blueprint for implementation. We have shown that it is theoretically impossible to use only homomorphic encryption to provide a sufficient set of operations for data in common real-world applications. To solve this problem, we extended and combined homographic encryption, Byzantine fault tolerance and dynamic adaption. Our developed set of algorithms were refined for efficiency and are specifically based on learning with error in polynomial rings. Trapdoor functions are used to allow zero knowledge verification, which reduces both space and time complexity.

In addition to the developed algorithms, we implemented the comparison circuits and chose one that offered the lowest time complexity. We observed an interesting tradeoff between time and space complexities: with a small amount of pre-computing and increased space complexity, we found that we could reduce time complexity. Therefore, when we detect increasing threat levels, we should increase the threshold number of machines into which an attacker must break in order to compromise data confidentiality. Thus, we devised a method by which as long as the number of machines that attackers break into is less than the current threshold, the system could adapt to increase the threshold, preserving data confidentiality.

Also during FY 2015, we produced a set of experimental measurements that quantify the overhead introduced by our proposed solution and determined the set of acceptable overhead thresholds, which established the targeted level of performance to make our scheme practical. We investigated a few techniques in improving the efficiency of resilient privacy assured computation, relying on ciphertext packing in reducing overhead. With ciphertext packing, permutations are often needed to rotate the positions of plaintexts for them to interact with each other. Permutation of plaintext positions is mapped to the permutation of coefficients of polynomials that use ciphertext packing to encode the plaintexts. Moving data around not only introduces overhead but also can cause unaligned memory access and pollute caches. We developed the mechanisms of virtual permutation to address this issue. Virtual permutation includes two mechanisms, one of which is indirection, allowing us to translate memory access to a different location. Another mechanism change references in the algorithms themselves. With virtual permutation, we can reduce data movement, which can reduce memory access, the major overhead in resilient privacy assured computation. Finally, we examined how to exploit application-specific data semantics to improve efficiency. For this effort, we designed a protocol to allow dynamically changing the threshold in the face of increasing security threats. We developed a scheme that allows us to mix ciphertexts with plaintexts. This scheme reduces the amount of memory or disk space needed to store the data and computation overhead. Moreover, we also reduced the increases in noise level. By reducing noise, we can reduce the number of bootstrapping and further improve efficiency.

From our work in this project, we published a paper in a DOE-sponsored workshop that potentially aligns us for additional proposals.

PN15036/2711

KRITIKOS: Identifying Cyber Assets and Assessing Criticality in Terms of Business Processes

Thomas E. Carroll

KRITIKOS provides continuous, (near) real-time enterprise introspection for discovering cyber assets, identifying the functional relationships and dependencies between assets, and assessing the importance of the assets to business processes that they serve.

Computer, network, and cybersecurity practitioners sense-make and decide based on information communication and technology aspects; as a result, decisions are generally void of an enterprise's manifold business objectives and processes. The lack of business operations information hinders the defenders' sense making, assessment, and management of situations. Current practices for identifying assets and mapping functional relationships are generally characterized by laborious, time-consuming, and error-prone processes that are difficult and expensive to deploy in large, dynamic enterprise environments. By linking business processes with their supporting cyber assets, KRITIKOS enhances cyber defenders' awareness and improves the quality and speed of situation assessment and management that align cyber security with enterprise objectives. Networks exist to serve business; in turn, business should inform the criticality of the network and its constitutes.

KRITIKOS functions as follows: a network model of the functional associations between services is constructed by discovering recurring temporal structure patterns in network flow information, common embedded instrumentation for the collection, characterization, and export of network traffic flow information and statistics. These recurring patterns arise from human-initiated machine-to-machine interactions that occur in the everyday operation of the enterprise. A business model that has processes annotated with essential services is correlated to the network model to identify other process essential assets. Asset criticality is then measured as a function of business process importance.

Our work in FY 2013 focused on developing a self-organizing map-based (SOM) algorithm to discover recurrent temporal patterns. SOM is a cognitive-inspired, unsupervised artificial neural network machine learning algorithm that "clusters" and "generalizes" by spatially organizing similar data in neighborhoods and dissimilar data in different neighborhoods. Recurrent temporal patterns arise as a result of functional dependencies between services. Service A depends on service B if a failure, disruption, or degradation of B reduces access, degrades performance, or somehow impairs the performance of A. These associations can be observed as paths in graphs or as temporal structures in which the interaction between entities are interrelated by relative time. Limited testing of the algorithm on the CyberNET testbed showed promise.

During FY 2014, we explored recurrent spatio pattern properties of NetFlow data. We designed a deep learning workflow to extract the patterns that coordinate multiple machine learning algorithms. The workflow begins with NetFlow data windowed and discretized. The input is provided to a SOM, which identifies potential patterns. After labeling landmarks within the SOM output, hierarchal clustering and decision support trees are used to extract association patterns robustly. Limited evaluation of the approach demonstrated greater applicability on the datasets generated in FY 2013. Another effort was investigating how to assess criticality of business processes. We developed an algorithm for computing criticality over the structures computed by the functional association discovery phase, assuming well-behaved existing business process modeling. Once criticality is assigned to a node, criticality flows from the node to its dependents.

For FY 2015, we developed an ensemble model of signal processing as well as statistical and machine learning approaches to discover and track dependencies. No longer does the SOM directly process incoming flow but is instead deployed on top of this new algorithm. The new approach has advantages over the SOM-only algorithm: it is amendable to streaming data, scales well with respect to flow volumes, and is robust to jitter and other data dispersion characteristics. The algorithm is described as follows: NetFlow are categories by a rule set based on networking principles, along with clustering performed by a simple machine learning algorithm. Records are then modeled as point processes, projecting them into an abstract event space. An ensemble model of co-occurrence detection methods examines sets of categories for temporal structure relationships. Finally, the set of co-occurring categories are assembled into recurrent temporal patterns, a robust temporal structure representation. A proof-of-concept was developed, and we conducted a study to evaluate the effect of flow volumes on the performance of passive network dependency detection. Using the CyberNET testbed, a test harness randomly composited 60 servers into services. User simulation interacted with services, generating NetFlow. Comparing our algorithm against other passive network-based methods found in the literature, we demonstrated that our algorithm was robust, while others were impaired by varying flow volumes.

PN13039/2520

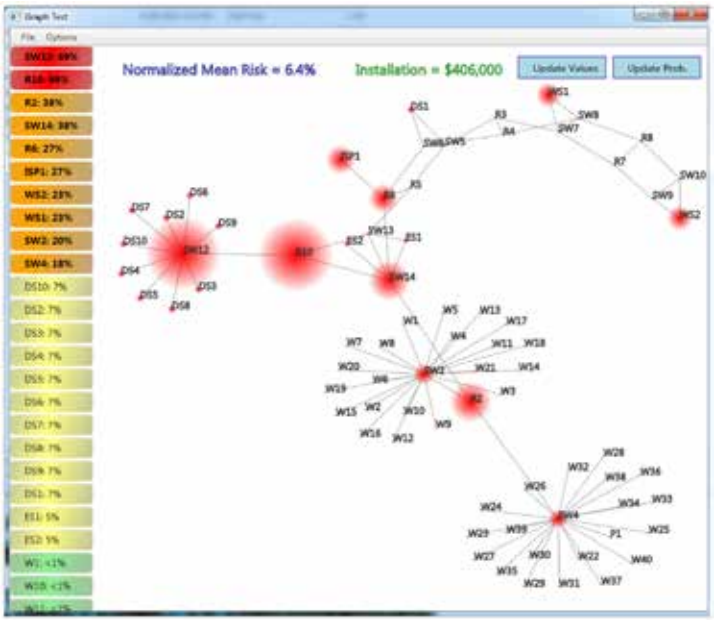
Leveraging Power Grid Contingency Analysis Techniques for More Resilient Cyber Networks

Mark J. Rice

Our aim is to leverage the contingency analysis concept as it has been developed for power grids and apply the technique to cyber networks so that the technique is practical in real world situations.

Although many metrics have been proposed to quantify the current "health" of a cyber system, few examine how resilient that health remains when one or more potential contingencies occur. Because computers and accounts are often compromised (many times without the operators' knowledge), it is important to know if the system remains healthy despite these compromises. Power grid operators use a technique called "contingency analysis" to deal with this. Our goal has been to apply this basic concept to the cyber domain to determine whether systems can be made to be resilient against potential contingencies before they occur, giving a potential asymmetric advantage to the defender.

Our research began with building an availability approach to cyber contingency analysis highly influenced by the practice of power grid contingency analysis. To perform this test, we iterated over each contingency node and removed it from the graph, checking to see which mission critical paths can no longer be made in the network. We add the value of the node removed and the paths broken to determine a severity score for that contingency. These values were then used to compare against hypothetical alternative system configurations for improvement, allowing for a similar analysis to what is currently done for power grids.



Our visual analytics prototype for availability contingency analysis. Risk for each contingency is listed on the left-hand side, with total risk at the top. Color is used to represent areas of greater risk.

In addition to the contingency analysis, we developed approaches for confidentiality and integrity. All users accounts were calculated to see which confidential files to which they have either or both read or write access. The number of sensitive files is summarized for their respective confidentiality or integrity severity score. Likewise, a probability of account compromise can be used to calculate a confidentiality or integrity risk score by multiplying it by the respective severity scores. As before, collective severity and risk scores are calculated by the sums of the scores for individual contingencies. By experimenting with user and group permissions, an operator can reduce the collective severity scores for confidentiality and integrity concerns to improve system resiliency against one of its accounts becoming compromised. The less damage that any particular account might provide, the more resilient the system should be against attacks.

A version of our confidentiality and integrity approach was implemented that can be used on users' personal systems. This system looks at all the users who have logged in as well as all the groups that exist on it. It can then provide the risk and severity for both individual accounts and the groups to which the users belong. An analyst can use this information to discover why particular accounts may be more risky than others and determine the best mitigation. The tool features a user friendly interface to make it easier for staff members wishing to test this system. Our hope is to see whether this tool can be used to prevent real confidentiality and integrity concerns at PNNL by the users who test the software.

During FY 2015, we completed our scientific experimentation of the availability tool. The experiment was performed using Common Open Research Emulator (CORE), a model that that executed a simulated denial of service attack on the system to confirm that our hypothesis in cyber contingency analysis was correct. We also worked to refine our two tools developed in the first year: a graph-based availability contingency analysis tool and an account discovery tool that can be used to ensure that the least privilege concepts are followed. The enhancements include the ability to fine tune the weights given to information or missions being impacted, and the installation of a graphical user interface for both tools.

PN14024/2608

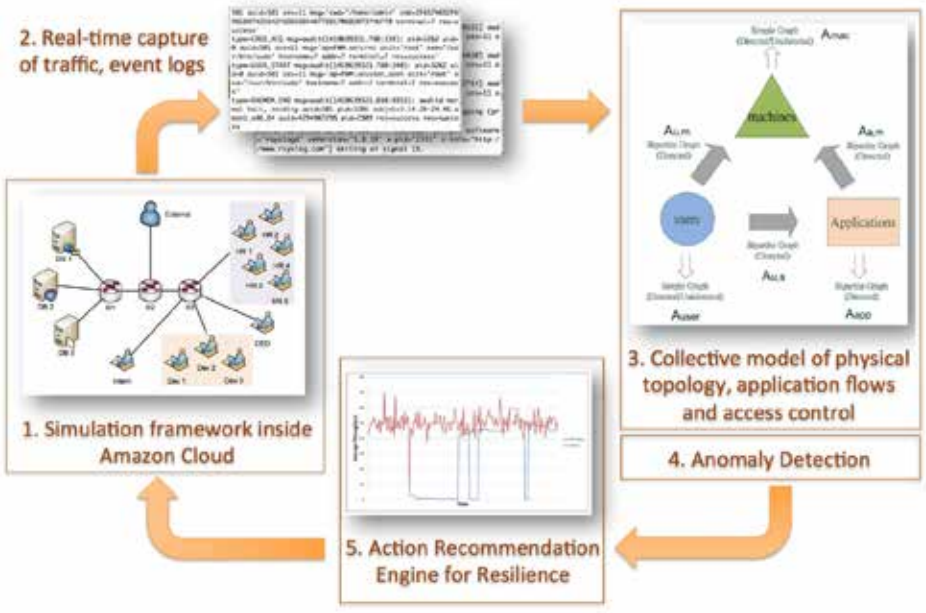
M&Ms4Graphs: A Multi-Scale, Multi-Dimensional Graph Analytics Framework for Cyber Security

Sutanay Choudhury

This project is delivering a set of scalable, uncertainty-aware, multi-scale graph analytics tools for cyber analysts and mission defenders.

The current approach toward mission assurance and cyber defense is primarily reactive. Automatic discovery of critical missions and their relationships with users, applications, and the physical infrastructure is a major challenge. Thus, chartering the response to a security incident is a manual process with high complexity and uncertainty. In addition, a cyber system is constantly evolving and generates prodigious amounts of data. Therefore, a scalable framework to provide continuous updates of the system state in terms of important security metrics is absolutely critical.

This project is taking a graph theoretic, data-driven approach toward modeling the dynamic behavior of a cyber system at multiple scales that range from a single machine to an entire enterprise. The models will provide continuous metric based updates to provide situational awareness and enable a system that is resilient by design. Specifically, we are modeling the key behavioral aspects of an enterprise by studying the information flow across hosts as large-scale, dynamic graphs.



Our software framework and process

We adapted a novel, multi-scale approach for continuously updating the graph-based model with local information and enable very fast computation of essential security postures and cost/benefit metrics. By accounting for both the connectivity structure of the graph (who talks to whom) and the attributes of the communication (using which protocol, how often, and for how long), we are able to create a comprehensive model that describes the behavior ranging from micro- (host) to macro-scale (enterprise). Our approach allows for ingesting multiple data sources such as netflow, event logs, vulnerability information, and similar types into one model. We can then reason about actions in the model space before employing transformed actions that were determined for that space. For example, deleting a graph edge in the model space is akin to blocking rogue communication between two machines in the real world.

Specifically, we developed a software framework with several unique features, including a graph-based model construction from cyber data sources (i.e., event logs and network flow). It contains a library for computing graph-based resilience metrics for structural susceptibility, measuring a system's dependence on the availability of a few critical entities; robustness to privilege escalation (e.g., how amenable is a system to lateral-movement based attacks?); and with indicators for structural and behavioral changes or anomalies. Additionally, the framework contains a software simulator to create a system instance with specified user access control and application profiles. Finally, the framework has a recommendation engine to stop or migrate a service based on emerging behavior as well as the ability to change access control or block applications to improve system resilience.

During the last year, the work under this project has been presented at four (and potentially two additional) conferences and, as of the end of FY 2015, a manuscript is in preparation for submittal to a peer-reviewed journal.

PN13037/2518

Module Integration Interface for Resilient Cyber Systems (MiiRCS)

Jeffrey L. Jensen

MiiRCS is a specialized software integration architecture that provides secure data transport, sharing, and routing to cyber security applications that act in a larger integrated solution to achieve greater resilience in the enterprise while in a compromised state.

Our project focuses on two areas supporting the demonstration and measurement of a resilient enterprise. The first emphasis is on integrating research (and possibly other third-party) applications to operate in the initial stages of the cyber decision cycle. These applications perform various functions that can support resiliency and mission preservation while under attack. There are several common enterprise integration patterns from which MiiRCS has adopted an asynchronous messaging architecture using Java Enterprise Edition (EE) and the Java Message Service (JMS) application programming interface (API). This process allows potentially any of the research applications to integrate in a loosely coupled, distributed fashion to overcome issues surrounding remote communications such as unreliability, latency, and availability. The second area is a search and evaluation of existing tools, technologies, and applications that could be added to our integrated solution. There are many applications with the potential to operate alongside this research to increase resiliency; thus, our project has begun documenting and ranking other research and applications from commercial, other government, and academic institutions for potential use in FY 2016 demonstrations.

During FY 2015, we created an initial prototype integration software architecture based on Java EE and the JMS API, including four reference implementations (or example applications) integrated in the overall software architecture. There are two behavior applications that operate on syslog and netflow data to establish normative behavior for individual clients in the network. This behavior is constantly updated and made available to other applications via the integration architecture. The two models operate in the discover phase of the decision cycle. A separate application operates in the decide phase and "listens" to behavior data. According to logic programmed in the decider, when the behavior deviates from normal, commands are broadcasted to multiple firewall client applications distributed in the enterprise. These firewall applications operate in the act phase of the decision cycle and have the ability to adjust firewall rules and increase logging based on commands received from the decider. All application communications are routed and delivered via the MiiRCS integration architecture using JMS. Specifically, each behavioral application was started and trained on normal syslog and netflow data. Data were then pushed through each model that caused the decider to recognize a deviation and command the firewall applications to drop traffic to potentially compromised machines in the network. This exercise validated our initial decision to use Java EE and JMS to implement an asynchronous messaging architecture enterprise integration pattern to meet specific requirements. We also started to integrate software applications from two other research projects.

In total, we evaluated over 30 existing technologies that could potentially complement research and increase resiliency. Several candidates were eliminated, as many were found to be notional and had no usable software. Others were proprietary and not obtainable for research purposes. Of the 30 plus technologies, eight warrant further evaluation in the next year, many of which are variants of moving target defenses. Some are commercial products, such as Palo Alto Network's advanced firewall appliance, while others are research from other national laboratories or academic institutions.

A mid-year demonstration brought to light the increased need to provide a more secure integration architecture that could protect the network it is operating in more reliably. Given that requirement, our team is actively studying other integration architectures and evaluating their security measures, even in light of those systems being based on different requirements than those of PNNL's Asymmetric Resilient Cybersecurity initiative. Ultimately, the choice to use Java EE with JMS inherently lends itself to developing a moving target defense solution on the integration architecture itself. Java EE and JMS are standards, and there are dozens of compliant implementations of each, meaning that the integration software itself is capable of running on any compliant Java EE container, any JMS provider, and any major operation system.

In FY 2016, the MiiRCS project intends to investigate an agent based framework actively being developed by researchers from Florida Institute of Technology. Our team will also look closely at a Canadian government-sponsored solution for automated cyber defense that exhibits many common goals and characteristics of our work. We will continue to evolve the prototype integration architecture in support of a new demonstration project that will assemble the most relevant applications in various phases of the decision cycle to demonstrate resiliency in the enterprise while in a compromised state. Our project will support this effort by creating the necessary integration points in the architecture. The system can then be deployed in the testbed, into which applications can be evaluated under numerous attack scenarios.

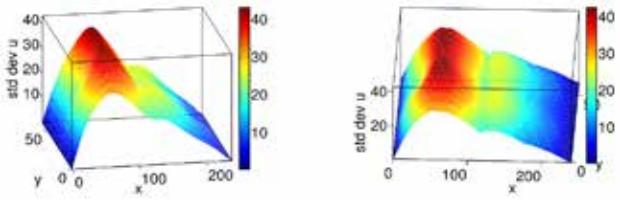
PN15076/2751

Multiscale Modeling and Uncertainty Quantification for Complex Non-Linear Systems

Alexandre M. Tartakovsky

Our research is creating novel dimension reduction methods for large size, non-linear systems of deterministic and stochastic equations, potentially leading to an explosion of results in mathematics and various engineering and science applications.

We are developing multiscale models for complex non-linear systems. Our general idea is that one needs to exploit as much as possible the inherent structure of a problem before engaging in computations. Features such as time and/or scale separation, variable and component dependencies, and randomness should be used as guides to reduce the actual computational work. At the same time, the need and usefulness of the elegant formulations that encompass many different cases should not be ignored: they allow us to view the big picture, make connections between seemingly unrelated subjects, and serve as starting points for controlled approximations.



Standard deviation of the solution of the stochastic diffusion equation. Left: exact solution; right: solution obtained with the basis adaptation method.

Mesh refinement. We constructed a unified framework for mesh refinement in physical and random spaces. The physical space mesh refinement is required in problems in which several fine features develop as a solution evolves in time and/or singularities are formed. In the random space, mesh refinement is required when a problem depends on many random variables but is sensitive to a few of them or also when the solution exhibits discontinuities in random space. For all of the above cases, the key underlying mathematical feature is the need to predict accurately the rate at which activity (energy, mass, and the like) is transferred to smaller scales. To this end, we constructed a computational device that uses ideas from model reduction to estimate the rate of activity transfer that can apply the approach to non-trivial problems. The results have been encouraging, particularly in the study of nonlinear partial differential equations with complicated physical or random space behavior.

Stochastic basis adaptation for uncertainty quantification. We are using a polynomial chaos (PC)-based uncertainty quantification method to solve partial differential equations with random coefficients. Such equations are commonly used to model heat conduction in randomly heterogeneous materials and fluid flow in subsurfacs, among other natural and engineered systems. Standard PC methods suffer from the so-called curse of dimensionality, referring to the fact that the computational cost of PC methods increases exponentially with the number of random variables needed to characterize random inputs. Because of this situation, the use of PC methods is limited to problems with smooth parameter space that can be represented with only a few random variables.

In this work, we are addressing the curse of dimensionality by using the basis adaptation representation of random space for sub-domains of interest. We demonstrated that the adapted space can be significantly smaller (in terms of the number of random variables) and the governing equations can be solved much faster than the original problem. The resulting solution is highly accurate within the sub-domain of interest and is less accurate outside of the subdomain. If solution is needed in the entire domain, then it can be discretized in several subdomains, and our approach can be used to obtain solutions in each subdomain. Finally, the solution in the entire domain is obtained as a superposition of the sub-domain solutions. The figure shows the exact solution and the solution obtained with the proposed approach. In this problem, the operation count to obtain the exact solution is 8761 but is only 1541 in our approach, while the maximum error does not exceed 5%.

Smoothed particle hydrodynamics (SPH) model for high energy density lithium (Li) batteries. Dendrite formation on the electrode surface of high energy density Li batteries causes safety problems and limits their applications. Suppressing dendrite growth could significantly improve Li battery performance. Dendrite growth and morphology are functions of the mixing in the electrolyte near the anode

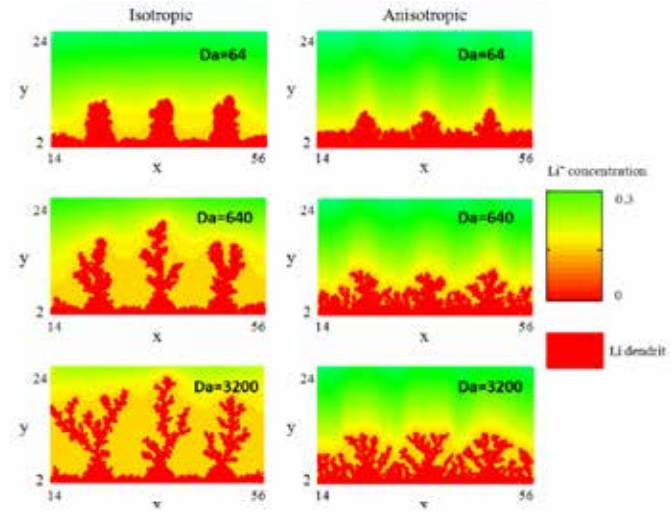
PN14089/2673

interface. Most research into dendrites in batteries focuses on dendrite formation in isotropic electrolytes (i.e., electrolytes with isotropic diffusion coefficient).

In this work, an anisotropic diffusion reaction model is developed to study the anisotropic mixing effect on dendrite growth in Li batteries using the SPH method to model dendrite growth in an anisotropic electrolyte solution. The model is then verified by comparing the numerical simulation results with the analytical solutions, and its accuracy is shown to be better than previous particle-based anisotropic diffusion models. Several parametric studies of dendrite growth in an anisotropic electrolyte were performed, and the results demonstrated the effects of anisotropic transport on dendrite growth and morphology, showing the possible advantages of anisotropic electrolytes for dendrite suppression.

Incompressible smoothed particle hydrodynamics (ISPH) for large-scale simulations. In this work, we used a consistent second-order ISPH implemented with the massively parallel particle library LAMMPS and the linear algebra library Trilinos. LAMMPS is used to provide a computational framework for large-scale particle-based simulations such as domain decomposition, load balancing, (re)neighboring of particles, and communication of particle-associated data fields. The implicit time-integration was completed using the Trilinos solver.

In FY 2016, we will couple ISPH with the SPH model for dendrite precipitation and electrostatics to simulate batteries under more realistic conditions.



SPH simulations of Li dendrites growth in Li batteries with "isotropic" (left) and "anisotropic" (right) electrolytes.

Network Chimera

William J. Hutton

Our network simulation environment was used as a proof-of-concept for various resiliency theories, including temporal diversity and investigating these theories' higher order effects.

The chimera is a mythical beast composed of a lion, dragon, goat, eagle, and snake. At times, modern enterprise infrastructures similarly consist of hodgepodge pieces combined, often in unplanned ways – a wifi hotspot here, administrative access for the high level professional there – and very quickly this structure (or lack thereof) creates a system where robustness is lost. This project applied theories of robustness to evaluate infrastructures and used those results to create new, more robust infrastructures. When attempting to design robustness into an infrastructure, there is no high level logical method. Low level robustness (policies, limitations, and the like) are implemented, but the high level architecture and design fail to consider robustness, and a majority of other work looks at specific threats and vulnerabilities. Our focus was more comprehensive, looking at the overall architecture of the infrastructure and how components altered the big picture. We attempted to identify robustness-positive vs. robustness-negative factors that could include specific components policies and network architectures. Our approach divided the research into two parts – testing of both existing architecture styles and newly created network architecture models based on prior results – to evaluate the various factors, their interactions, and how these affected robustness.

The Chimera, symbolic model of our project name

One of our most important findings in FY 2014 was the discovery that concurrent component diversity will likely negatively impact the overall resiliency of a network, but temporal diversity or diversity over time will likely positively impact network resiliency. During FY 2015, we investigated the impact of temporal diversity on resiliency. We studied how temporal diversity is widely beneficial against grey threats (the environment) but largely iineffective against red threats (adversaries). The effectiveness of temporal diversity against blue threats (trusted users) was not evaluated. For specifically dealing with grey threats, application fault tolerant middleware such as Adaptive Reconfigurable Mobile Objects of Reliability ("Armor") have been deployed in the financial sector (NYSE), commercial aviation (ARTCC), and space exploration (NASA JPL). An application such as the Trusted Dynamic Logical Heterogeneity System ("Talent") provides a framework for live migration of applications across heterogeneous platforms to increase diversity and limit the impact of any vulnerability for a particular system stack. Portable checkpoint compilers can also be used to migrate process states, as their maintenance is critical to making temporal diversity transparent to users, especially across heterogeneous architectures (e.g., 32-bit vs. 4-bit, big endian vs. little endian, etc.).

Two key areas of future research were identified: reducing the complexity of implementing and using temporal diversity; and the discovery and removal of barriers to implement a security or resiliency tool. Implementing temporal diversity is difficult and expensive. Additional research is required to make implementing temporal diversity easier and more transparent to users to increase the adoption of temporal diversity. The disadvantages of heterogeneity must reach parity with the advantages of homogeneity for diversity to be considered.

As cyber security researchers, it is imperative that we not assume defenders are already doing everything they can defend their systems and networks. Often, it is not new tools that are needed, but the correct application of existing tools. Defenders cannot gain an asymmetric advantage until they have a symmetric advantage. More must be done to understand why existing tools and best practices are not implemented (e.g., encryption to ensure confidentiality, redundancy to ensure availability, etc.).

PN14034/2618

NOUS: Incremental Maintenance of Knowledge Graphs

Sutanay Choudhury

The primary outcome of this project is a large-scale knowledge graph system that evolves over time and will be useful as a conjunctive tool for the domain expert to create and validate hypotheses.

Artificial intelligence has made tremendous progress over past 50 years. However, we are still far away from the point at which the intelligence of a computer system is comparable to a human being. Computers having the abilities such as exploiting pre-existing knowledge, learning from experience, and discovering new knowledge are important traits to possess for achieving the level of human-like intelligence. In this way, data-driven applications critically depend on human experts who learn about a given domain through their interaction with data over time: the persons gain experience and familiarity with the domain. The surge in data volume, throughput, and diversity pose newer challenges for training experts. Codification of domain requisite knowledge for classification and reasoning is not sufficient; the persistence of knowledge as well as the experience of the human expert are critical.

The term "knowledge base" has been around since the early days of artificial intelligence and expert systems research. One may think of knowledge graphs as knowledge bases storing facts about inter-related entities, where entities may refer to people, organizations, locations, or even words or scientific topics. Knowledge graph construction and maintenance are expensive processes that involve manual curation by domain experts. Such approaches become infeasible as data sources grow in volume and variety, creating and motivating the need to explore automated approaches that scale with these data sources.

In this project, we are constructing large-scale knowledge base systems that evolve over time. We refer to the knowledge base as knowledge graph due to its representation as a graph data structure. Specifically, we are focusing on three science questions:

- How do we learn the ever-evolving set of patterns or rules for a domain from a data stream?
- How do we determine the veracity of facts that arrive in a stream?
- How do we infer new facts by observing the stream of information?

In FY 2015, we developed a scalable prototype that incrementally constructs a knowledge graph from large text streaming data such as *The New York Times* and *The Wall Street Journal*. A visual model of the process is included as a graphic depiction in the image. In addition, we developed and implemented an algorithm for incrementally discovering patterns from a stream of tuples.

Knowledge graph construction pipeline

The knowledge graph stores information about various entities and the strength of their association. We developed a link-prediction based approach toward determining the likelihood of a new fact that is based on prior known facts. Additionally, we developed and implemented a graph reachability-based algorithm for generating explanations for hypotheses. Given a query such as "why does Honda import Nickel Hydride batteries?," we can generate an explanation such as Honda is an automotive company, automotive companies use fuel cells, and nickel hydride batteries are used in fuel cells. For our efforts this year, we submitted a software invention disclosure for the system prototype and are preparing for an open source release to the research community.

During FY 2016, we aim to scale up the knowledge system in the cloud, reporting scalability and accuracy performance with respect to state-of-the-art benchmarks. As an initial prototype for user interface, we will introduce the feedback module for human-in-the-loop. Finally, we will prepare end-to-end demonstrations for selected domains.

PN15023/2698

Online Predictive Analytics on Streaming Data

Bobbie-Jo Webb-Robertson

The goal of this project is to develop a methodology for event detection and characterization that achieves high accuracy and speed in dynamic and high volume domain spaces.

Many real-world applications involve aspects of dynamic control, data mining, and classification in feature spaces that are drifting over time. Current technologies provide the ability to collect large amounts of data in real time, offering the potential for major advances in dynamic data-driven decision-making. In these cases, ideally training examples are incrementally generated, made available, and then fed into evolving models. The benefit of such an approach is that it mirrors how humans assimilate knowledge in a piece-meal fashion over time. However, current predictive models are limited in their capacities to ingest large-scale and/or high velocity data, deal effectively with missing or incomplete data, and detect rare events.

This project aims to locate events of interest in a set of data that is changing over time. It will do so by using a time-evolving method that can also describe and localize changes to the underlying dynamics of the system, which will be exploited to provide enhanced knowledge of complex systems. To provide this functionality, this project will explore the use of an automated structure that has incremental machine learning in a time-varying method, the use of variations in behavioral models to establish the indicators of changing dynamics, and the use of missing or hidden variable methods to drive future data collection. Our goal is to close the gap between the potential and the realization of incremental machine learning to allow for *in situ* decision-making on streaming data.

For this project in FY 2014, we conceptualized the Dynamic Incremental Machine Learning Model for Evolution (DIMME). Within DIMME, we evaluated multiple machine learning algorithms for the potential to deal with non-stationary data in the framework of a spectral processing use case. In this context, algorithms were evaluated based on the capability to classify chemicals correctly, with known characteristics occurring simultaneously within a single spectrum with variables in both overlapping peaks and unknown shifts and concentrations. Several machine learning algorithms, some of which were integrated with inductive models, demonstrated the perfect classification in our initial experiments involving a small number (between 3 and 10) of simultaneously occurring chemicals. The identification of algorithms with the most potential to scale for use in a streaming spectral context was then completed for data involving 50 to 100 simultaneously occurring chemicals. Results showed that traditional machine-learning algorithms were not sufficient to classify many chemicals effectively in this more realistic context.

In FY 2015, the DIMME framework focused on quantifying and identifying model evolution to determine when the incremental learning paradigm should regenerate models in near real time. In the spectral processing use case with between 50 and 100 compound libraries, a support vector machine algorithm was coupled with a functional data smoothing spline algorithm to identify compounds incrementally, estimate abundance, and remove compounds from a sample. Results showed a better classification performance for the incremental learning algorithm compared with the non-incremental method. The incremental algorithm is also amenable to the development of a paradigm that allows for the identification of unknown compounds in an observed spectra.

Also in FY 2015, a shipping records use case was used to demonstrate an incremental naïve Bayes model. Under this case, the goal was to detect changes in a line of business for a company based on its shipping records. It was demonstrated that the incremental naïve Bayes model was more effective in classification than the traditional machine learning algorithms. A method for measuring model drift to quantify and characterize model evolution was formalized based on the relative distance metrics and ranks of these metrics amongst posterior distributions of model features.

PN14063/2647

Rendezvous: Optimization and Stochastic Algorithms for Asymmetric Resilient Infrastructure

Mahantesh Halappanavar

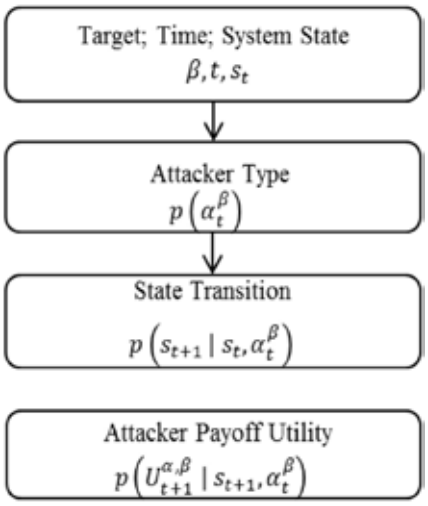
By developing a framework for uncertainty quantification of attacker payoff utilities in this project, we enable the application of game-theoretic methods for improving the resilience of cyber systems.

Cyber security is a multifaceted, challenging research problem. Game theory provides a mathematical framework to model and analyze dynamic interactions between multiple agents (e.g., attackers and defenders). Game theory has therefore been applied to solve several cyber security problems such as intrusion detection and network interdiction. However, the application of game-theoretic methods is significantly limited by uncertainties in attacker payoffs and accurate identification of system states.

Game theory is the mathematical study of the interaction between two or more entities acting to achieve their individual goals. Game theoretic methods have been successfully applied to solve several challenging problems related to cyber security. However, a significant limitation of current approaches is the lack of rigorous treatment of uncertainties in payoffs and system states. A thorough investigation of uncertainty quantification methods applied to cyber security games will therefore benefit the cyber security research community and help advance the state-of-the-art in this domain. Previous research in the area of uncertainty quantification in physical security has focused on representing the defender's beliefs about attacker payoffs as point utility estimates. More recently, attacker payoff uncertainties have been represented as Uniform and Gaussian probability distributions, and intervals. Within a cyber security setting, continuous probability distributions may still be appropriate for addressing statistical (aleatory) uncertainties where the defender may assume that the attacker's payoffs differ over time. However, systematic (epistemic) uncertainties may exist, where the defender may not have sufficient knowledge or there is insufficient information about the attacker's payoff generation mechanism.

Cyber attacker payoffs are subject to various sources of uncertainty, including attacker types and their attack plans and the state of the system. These uncertainties may be aleatory or epistemic in nature, depending on the level of available information and knowledge about the attackers and the system. The objective of our framework is to estimate the probability of attacker payoff utility for a certain target and level of protection. There are four elements in this framework: 1) baseline conditions (including a target with a certain level of protection, at a given time; and the state of the system); 2) probability density of attacker type; 3) probability density of state transition at a time step immediately following the time of attack; and 4) probability density of attacker payoff utility. These payoff probability distributions or intervals are intended to inform the stochastic security game model. For example, given an attack graph representation of a cyber-system, optimal strategies for a defender can be computed using a stochastic game (Markov decision process).

In 2015, we developed a framework to quantify uncertainties in the cyber attacker payoffs. To validate the techniques proposed, we developed a prototype implementation and tested using a small representative cyber system. We published the work in the IEEE Symposium on Technologies for Homeland Security in April and were the recipients of the best paper award for the cyber security track. Additional key contributions of our work in 2015 were the representation of dependencies among attacker types, target protective conditions, and system states as conditional probabilities; development of a probabilistic framework to reason attacker payoff uncertainties; and identification of uncertainty quantification methods to address sources of aleatory and epistemic uncertainties in the attacker payoffs.



The above image illustrates our uncertainty quantification framework and presents a mechanism for propagating uncertainties throughout the modeling process to arrive at the probability of attacker payoff utility.

In 2016, we plan to continue our work in three areas. Our first focus will be on uncertainty quantification using a conditional probabilistic reasoning to organize the dependencies between a cyber-system's state, attacker type, player actions, and state transitions. Optimal network interdiction methods will be employed to include uncertainty using bounded rationality for attacker actions. Finally, optimal defender responses to zero-day type of attacks using simultaneous games will be used to address insufficient information.

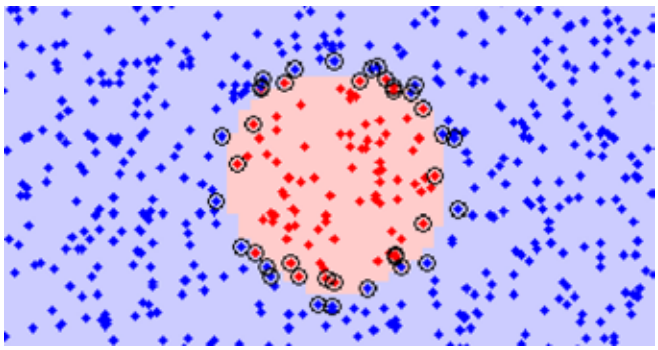
PN15031/2706

Scalable Feature Extraction and Sampling for Streaming Data Analysis

Abhinav Vishnu

The objective of the project is to design a set of large-scale parallel sub-sampling algorithms for execution on cloud computing systems and supercomputers.

Today, we are producing exorbitant volume of data using mobile devices, network sensors, scientific simulations, and other instruments. Machine Learning and Data Mining (MLDM) algorithms, which analyze these data and produce useful information such as classification models, are critical in science domains (such as distinguishing between signal and background for identifying the Higgs Boson particle) and cyber security regardless of whether a network system is under attack. With increasing volume and velocity, several attempts to design parallel MLDM algorithms have been proposed. However, not every data point is equally important. Usually, only a subset of data points define the model, yet most approaches use the entire dataset for model generation using Machine Learning. In addition, these approaches are geared toward batch processing of data even though we are ushering in an era in which data velocity is increasingly the primary issue. Upon in-depth analysis, we observed that there is a gap in parallel algorithms that incrementally sub-sample a high velocity stream and learn the model iteratively over the lifetime of the stream.



Our developed parallel SVM algorithm, processing samples and reducing the working set by observing a pattern.

Our project will provide a mechanism to address data velocity by learning model only a subset of data, while still gathering almost accurate information. Our research in feature extraction and sampling by using parallel computing systems will create a fundamentally new approach for analyzing very large datasets with potentially minimal accuracy loss. The project outcome will provide better models for science domains, human behavior, and cyber security. A specific expected outcome is an open source software that would be used by scientists and other researchers for faster and better scientific discovery.

We expect to build faster machine learning and data mining algorithms by using smart mechanisms for sample elimination (sub-sampling) and executing these algorithms using the computational features of architectures available today. As an example, modern systems consist of GPUs and MICs, which are rarely used in conjunction with the system core (such as Intel Haswell) and high performance network. We intend to build MLDM algorithms such as support vector machines (SVM), clustering algorithms, and deep learning algorithms, which are still in their infancy in terms of large scale. We expect that the impact of the existing project will transcend national laboratories and academia.

In FY 2015, we made significant strides in designing large-scale MLDM algorithms, which iteratively reduce the overall computation while maintaining the accuracy of the proposed solution. As an example, we developed a novel parallel SVM algorithm that eliminates the unnecessary samples from the computation. While several sampling algorithms reduce the cardinality randomly, the proposed algorithm processes the samples and iteratively reduces the working set by observing the following pattern, readily observed in many real-world datasets. As observed in the figure, only a few samples actually result in defining the boundary between blue and pink points. The proposed algorithm and its implementation using MPI with evaluation using up to 4096 cores shows its efficiency. Specifically, we evaluated the proposed algorithm using Higgs Boson dataset, and we observed that in comparison to the algorithm that does not conduct any elimination, our proposed algorithm can reduce the overall execution time by 2 times. We conducted similar evaluation with other real-world datasets in many domains, and the results were along similar lines.

We also designed and developed a novel parallel algorithm for frequent pattern mining. We observed that the algorithms proposed in the literature conclude that load balancing and

PN15024/2699

communication are the primary problems with the frequent pattern mining algorithms. Specifically, we considered the FP-Growth algorithm, now considered the default frequent pattern mining algorithm due to its low time and space complexity. We developed a work-stealing algorithm using MPI one-sided model and created a new method for merging distributed trees such that the overall communication time reduces by up to 38 times. We will be presenting this work at an IEEE conference.

For FY 2016, we are conducting extensive research in designing large scale MLDM algorithms. Specifically, we are interested in designing faster deep learning algorithms that have recently received significant attention from the research community. Our objective is to design multiple deep learning algorithms that reduce the model generation time and model size itself while maintaining the accuracy of the solution. Specifically, our initial analysis shows that deep learning algorithms may suffer from overfitting, which causes problems for validation. Hence, we are considering algorithms around elimination and dropout for better models.

As systems continue to scale, we are also observing that faults are becoming a norm rather than an exception. We plan to build fault-tolerant MLDM algorithms, especially ones that execute for long periods of time. We will specifically consider SVM and FP-Growth as examples for these algorithms.

Scalable Hierarchical Validation and Calibration for Robust Distributed Control of Large-scale Complex Systems Under Uncertainty

David W. Engel

We are developing and implementing carefully designed validation and uncertainty quantification (UQ) methods and toolkit-distributed control tools, models, and data for temperature sensor use in air conditioners, water heaters, refrigerators, and smart meters for buildings and distributed generation/storage.

Large-scale complex systems are often heterogeneous and under various physical constraints such as nonlinearity, saturation, and uncertainty. Approaches for validation, calibration, and uncertainty quantification (UQ) that are data-driven may be capable of providing estimates of uncertainty that are time-varying as the quantities being measured vary with time. Such a capability provides the option of adjusting acceptance criteria and potentially set points in a time-varying fashion to meet the needs of the control of the next generation of complex systems. The majority of control systems do not adequately quantify the uncertainties that occur within complex systems such as the power grid. The identification and quantification of the difference sources of uncertainty is needed because it leads to an estimate of confidence about the automated control systems.

In this project, we are developing a hierarchical layered strategy that will allow us to incorporate different uncertainty sources in a distributed or hierarchical control system (e.g., parametric uncertainty, model uncertainty, and data uncertainty) to assess how accurately the behavior of the distributed controller and computational results compare with the experimental data for different physical phenomena coupling and at different geometrical scales. To accomplish our goals, we are developing a general toolbox for uncertainty quantification, optimization under uncertainty, and model calibration.

Specifically, the control of complex systems under uncertainty contain four elements: control variables, uncertain parameters, objective quantities, and observable quantities. For uncertainty quantification, given a designed control strategy, we are studying how uncertainties in the system affect the objective. With optimization under uncertainty, design control strategies are used to optimize the objective by considering the uncertainties of the system (e.g., to maximize the expected objective). In data assimilation, we are calibrating uncertain parameters to observed data in order to reduce uncertainties (i.e., to estimate the posterior distribution). To help in our project development, we are applying our techniques to a specific example, a project that is market-based coordination of thermostatically controlled loads. Initial results from this example illustrate the benefits of the different techniques that we are developing.

In FY 2016, we are first planning to tie the UQ toolkit with other control models/capabilities, specifically control systems being developed as well as visualization tools and model architectures. We will incorporate data from the testbed and demonstration cases to implement advanced UQ methods, including model reduction (truncated Karhunen Loeve [SVD] expansion that results in a reduced set of uncertain parameters) and using more efficient stochastic optimization methods, such as generalized polynomial chaos (gPC) expansions to quantify uncertainty propagation from the input parameters to the object function and constraints. We will also use stochastic collocation based on sparse grid, nonlinear regression, or compressive sensing.

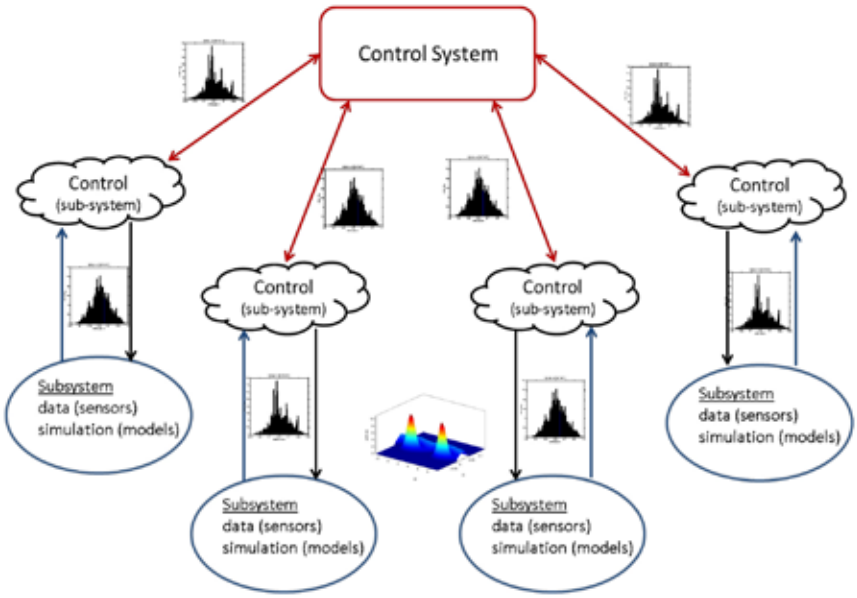


Illustration of a distributed control system showing the hierarchy and uncertainty propagation from the local subsystem signal (blue) to the local control signal (black) to the global system signal (red).

PN15002/2677

Scalable High-Level Programming

T. Edmond Hui

We will enable a broad spectrum of scientists, engineers, and analysts to apply modern parallel computing systems effectively to their everyday tasks – and to the ever larger data sets they examine – to free them from the limitations of desktop computers and thus improve the pace of scientific discovery.

Scientific programming for the bulk of practitioners is dominated by tools such as MATLAB, Python, or R, developed before the major architectural change from single- to multi-thread processors. Their key designs inhibit them from implicitly maximizing modern architectures. While there have been several attempts to extract parallelism automatically, key design choices have limited the practical impact. We believe that with the design for parallelism as a central goal, we can overcome these shortcomings and provide a new language with a comparable ease of use and extensibility but with far greater applicability to modern problems.

The focus of this research is to prototype such a language design and its key implementation techniques. Core contributions will include

- demonstration of an automatic parallel evaluation of a high-level modeling language suitable for scientist and engineer use
- reusable design patterns for evaluator-compiler interactions to support effective, efficient optimization of high-level modeling languages
- optimization techniques for specialization and optimization of dynamically typed language in an on-the-fly context
- description of type-system and compilation interaction to support extensibility of high-level modeling languages with system-level support packages.

During the first year of the project, we focused on building out the initial prototype infrastructure. We identified key features and syntax elements to handle the range of patterns common in scientific programming. This activity also focused on examining existing practices and surveying emerging patterns, particularly those around structured data that have become a common metaphor for "big data" problems. These patterns converted to the basis for design of both data concepts and language syntax.

In FY 2014, we built prototype parser, compiler, and interpreter for a large subset of the language. As is common for this community, the language is dynamically typed, and the great bulk of functionality is ultimately provided through libraries. The implementation aspects that impact library design were fundamental to establish and provided a baseline for understanding the analysis challenges. We co-designed the type system with the interfaces for the library, particularly focusing on the boundary between the core language and libraries written in foreign languages such as C.

A key design aspect of the language is controlling the features that lead to the loss of effectiveness for parallel execution. This situation includes basic call semantics and data structure properties. The library interface design is particularly rich in order to enable an accurate analysis in the presence of foreign functions and to guide developers of such libraries to exclude parallel-unsafe patterns. We established these interfaces and validated them with sample libraries, which include core array support and multi-precision math libraries.

Another key feature is the patterns around the iteration over data structures, which are both extensible to new data structures and not part of the core language that support parallelism. The design is novel in its support for a number of distinct iteration patterns, and the late binding of these patterns is supported by on-the-fly compilation. This structure was validated on core array-based patterns but is also shown to be effective for supporting high-level, multi-dimensional loop constructs.

Another achievement in the last year was prototyping the interfaces between the reference interpreter used to validate the semantics of the language and the on-the-fly optimizer that is ultimately responsible for extracting a parallelism as well as eliminating various overheads of dynamic type checking where possible. A key responsibility for the optimizer is recognizing the parallel algorithm patterns and analyzing the array use, which are common techniques in main stream languages. Validating through demonstration, these techniques will be the application in this dynamic, extensible language; further, automatic storage management techniques will not inhibit them. This part of the work is ongoing, but progress has been very encouraging, with the most basic patterns demonstrated as analyzable.

Toward the end of the project, we briefly considered the possibility of expanding the analyzable patterns and adding a capability to translate those patterns into codes that would be suitable for parallel execution.

PN14021/2605

Science of Interaction: Towards Human-Machine Co-Reasoning

Nicholas O. Cramer

We are improving human insight from data by making complex algorithms and models more accessible and adaptive through inference over user interaction data.

A cornerstone of visual analytics is fostering sense-making, a cognitive process of gaining understanding into data by testing one's own assertions and domain expertise against data. Thus, current approaches to incorporating the user's domain expertise into the visual and mathematical system is through user interaction explicitly steering the computation. This direct manipulation approach for user interaction has been successful for interactive information visualizations. However, a new paradigm for user interaction is needed; hence, we present Science of Interaction, which aims to maximize the roles of human and computation for reasoning at scale and speed to enable faster, more meaningful insights. We base this work on the user interaction paradigm called Semantic Interaction, which suggests a connection between the embodiment of the process through user interaction and the cognitive discourse that users have with the information. As a result, capturing tacit knowledge associated with the user interaction in a mathematically structured form can lead to more a more fluid cognitive process of discovery, thus faster, more meaningful insight.

This project is implementing new user interfaces from which we can gather user interaction, develop new inference strategies, understand sensemaking, and explore mixed-initiative visual analytic systems. To this end, we instrumented a spatial visualization called the Discovery Canvas in FY 2014 to capture user interactions such as movement, grouping, and labeling of data. It was adapted to handle multi-dimensional representations of documents records and spectral data such as those produced by nuclear magnetic resonance (NMR) or mass spectrometry instruments. Functionality was extended to support a more complete analytic task, providing a richer set of interactions. Several feature weight inference strategies were also designed and implemented within the system. As the user incrementally explores and analyzes data, the machine learns feature weights to reflect a current understanding of the user's interests. The evolution of these weights is logged and visualized over time; alas, the evolution visualization process appears to reveal a user's cognitive processes.

In FY 2015, we conducted a user study in collaboration with the Georgia Institute of Technology to gather interaction data to examine sensemaking behavior difference when a user is faced with streaming vs. static data. Analysis of the study data has shown distinct differences between user groups that suggests certain features for consideration in future streaming data analysis tools to support sensemaking. A manuscript detailing the results of this study is being submitted to an international human-computer interaction conference for 2016. In addition, with other internal projects, two demonstration user interfaces were created. In the Strategic Surprise use case, we demonstrated an integrated display of multiple models predicting company's line of business over time and visually explaining the rationale behind the algorithms. The NMR user interface demonstrated monitoring changes in algorithmically predicted compound abundances and allows a user to feedback training data to the algorithm. These two user interfaces were successfully demonstrated.

This project resulted in two significant business development outcomes. First, it created a venue that combined bioinformatics and visual analytics experience, resulting in a successful new visualization tool suite to support biology research. Second, a U.S. Department of Defense contract based on this project combines the components of several projects for follow-on work. Together, these achievements have yielded a success in delivering new science in sensemaking, open source and cross-project software demonstrations, and new business.

Strategic Surprise and NMR use cases

PN14064/2648

Scire: Scientific Process for Validation and Verification

Mark F. Tardiff

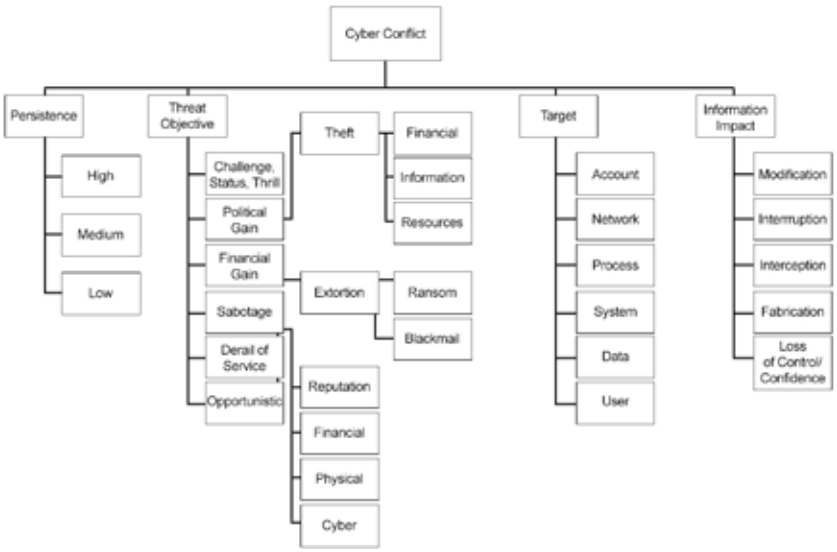
We are developing and exercising a methodology for verification and validation when performing modeling and simulation, experimentation and studies, and theoretical research.

Older, more established fields have generated foundational laws and theories upon which to base their engineered systems. However, cyber security still lacks necessary fundamental understanding of cyber space to engineer effective solutions. Cyber security needs to move beyond tradecraft and building interesting systems to include scientifically rigorous knowledge gathering and engineering based on science. Without a scientific approach, the status quo will remain; we will continue to be unable to differentiate fear, uncertainty, and doubt-derived mysticism from real solutions, and we will slide further down an asymmetric slope of attacker advantage.

To address scientific rigor within cyber security, we are developing tools that researchers will leverage to exercise their research questions, and we formed and are operating a science council to assist other projects in applying scientific approaches. Two scientific challenges that we found at the start of the project were the lack of a common reproducible approach to threat modeling and implementation for experimentation and the lack of adequate human initiated network traffic models to mimic human users in an experimental cyber environment.

This project's first task was to develop a cyber conflict taxonomy that enables the generation of threat models for testing in experimental environments. While the taxonomy provides a repeatable method of defining models of threats, it is still required to exemplify the threat model. A survey of threat activity was provided to gather possible methods that represent the defined threat models to be studied in different ways depending on the type of research performed. For instance, a theoretical evaluation of resiliency could generate functions from the threat model to explore fundamentally what would happen in the presence of different threats, during which a red team could be given the threat model to direct its actions in trying to achieve an objective in experimental research.

Our second task was to perform cluster analysis on real network datasets to derive human network behavior models. Experimental cyber security research must be performed within fabricated environments, but a significant gap in this research is a lack of realistic simulated users. Statistical cluster analysis was performed on anonymized PNNL network data to generate general models of human network behavior. These clusters defined mean behavior across a 24-hour period with variance bounds. From these models, simulated users could be studied that stochastically generate traffic within the bounds defined by the model. The method and models from this task offered a more realistic set of users that enabled more rigorous experimental cyber security research.



Cyber conflict taxonomy

To apply our knowledge, we formed a science council of experienced experimental scientists across many fields of study. This council developed a process by which it interacts with other projects to review their scientific questions and experimental designs to provide feedback and recommendations to improve rigor and effectiveness. The process included a subset of the guidance document developed in the first

PN13057/2538

year of this project with a set of questions that projects must answer in preparation for meeting the council. The goal was to have a solid research plan that has confidence in answering appropriate research questions. In FY 2015, the council engaged principle investigators on refining their research questions and hypotheses, experimental plans, and approaches for analyzing and interpreting results. Following an internal review, the council participated in developing demonstration plans for FY 2016 to show the impacts of a select group's technologies. The council has been instrumental is devising a plan to initiate a technology demonstration to allow for spiral development of integration, demonstration, and refinement. Additionally, the council continues to engage new start projects that are developing capabilities that will be evaluated for demonstration as those capabilities mature.

Shyre: Streaming Hypothesis Reasoning

William P. Smith

We aim to answer the question of what happens when hypothesis testing occurs automatically as new information becomes known.

Testing a hypothesis involves significant investigative effort, whether it is scientists performing experiments in a laboratory or detectives working to uncover illicit behavior. At the core of hypothesis testing is deductive reasoning, a gathering of relevant facts when combined with established background knowledge leads to useful conclusions. Although deductive reasoning is an established field in artificial intelligence, only recently has interest greatly shifted toward performing deduction at the time new information is received, termed stream reasoning. Information can be accumulated and processed later (offline), but this situation implies a significant delay between reception and the act of reasoning. Many works have focused on deduction over the most recently received information, but this approach has limitations because related information may not co-occur within the same window of availability. A new approach is to employ so-called data-aware eviction in which we actually try to remember (or forget) information selectively based on semantic content.

We are seeking to answer the following questions regarding data-aware eviction for stream reasoning to assess how information can be used in collaboration with other reasoning approaches:

- How do we structure the semantic technology stack to consume and reason over a volatile data stream?
- What are the effects of this configuration when expressing streaming data models through common-off-the-shelf (COTS) reasoners?
- How can deduction be used to quicken the investigative cycle of "human-in-the-loop" users?

In FY 2015, we continued the our research from FY 2014, but with significant modifications to the team and implementation of past research methodologies. Project plans were updated to remove the requirement for creating a custom reasoning platform and refocused on consuming streaming data. Specifically, we captured the use cases for two domains: nuclear magnetic resonance (NMR) and disrupting illicit nuclear trafficking (DINT). We obtained relevant background knowledge to support reasoning for problems in those domains and implemented a prototype stream reasoner using a custom cache data structure and COTS reasoners. We performed experiments on provided streaming datasets and demonstrated the efficacy of combining in-memory and triplestore support with reasoners supporting various levels of logical axioms.

Using the dataset provided by NMR teams the Pellet, StarDog, and AllegroGraph reasoners were provided streaming prototype simulations. The following modifications and results were recorded by reasoning platform for the NMR use case.

Pellet. The team presented findings of the in-memory Pellet reasoner NMR streaming tests to the scientific committee. Data ingestion from infrastructure could assemble NMR scans, the entire graph necessary for descriptive logic (DL) reasoning, in 45 sec. Queries on graph sizes ranging between 1698 and 1880 triples required 19 sec to detect the provided 30 chemicals encoded within the background ontology. Finally, when the scanned data was converted to a larger graph of ~20,000 triples, query times became 19 min, and all chemicals were detected in unknown quantities. Graph sizes below ~1730 triples significantly reduced the ability to detect known chemicals.

StarDog. The first triplestore test with streaming data was successful when ingesting and annotating data, but the supplied queries from FY 2014 were incompatible with the StarDog system, which requires a separation of TBox and ABox query parameters that were merged in the original query. Significant re-writes were required for the system to accept the query. The SNARL protocol StarDog to populate and query data within the triplestore performed quickly and effectively with only network latency acting as a blocker for increased data ingestion rates.

AllegroGraph. The second triplestore does not support the DL reasoning patterns originally created for the NMR use case in FY 2014. The team recreated the logical axioms using resource description framework schema (RDFS) reasoning standards requiring significant rewriting of the ontology, background data, and query. Due to query ranges of float variables required to detect chemicals within the spectrum peaks, queries were manipulated to support ranges, and the background 30 requested chemicals had to be recreated using RDFS specific logical axioms.

PN14065/2649

The team decided to generate programmatically companies designated as "exemplars," those with a long history of HSCODES that correspond directly to an industry. Examples of acceptable exemplar companies include Ford (automotive), Nike (athletic gear), H&M (clothing), and Walmart (superstore). Many import records corresponded with companies that would break the paradigm of exemplar organization such as General Electric and Toyota. These companies create products that cover many facets of modern industry and thus import a significant amounts of goods and materials that span many lines of business.

After exemplar companies were created as background information for the ontology, it now became possible to utilize DL reasoning axioms. These rules were used to compare and record an import stream while providing alerts as companies change lines of business based on the port import/export reporting service (PIERS) import data. However, two problems occurred when a live stream was being recorded and reasoned across. First, the original DL reasoning centered on keeping query axioms within an ontology (as opposed to within a SPARQL query), creating graphs that were too complex for DL centric streaming reasoning. We resolved this problem by simplifying the ontology rules and shifting logical axioms to the SPARQL query and data storage mechanisms. Second, streaming semantic cache maintenance remained an unsolved problem, but during the DINT use case, demonstration figures were presented that outlined the loss of processing power, as more imports were tracked across companies and business lines.

Records imported/Lines of business changes

Import Records	Output Results	CPU (sec)	CPU (inputs/sec)
10,000	15	77.619	128.834
20,000	88	185.553	107.786
30,000	129	330.895	90.663
40,000	168	508.902	78.601

As shown in the table's column "CPU (inputs/sec)," after an increase of input records by a magnitude of four, the CPU processing availability falls by 40%. As additional records are imported and tracked, the graphs become so large that a query between importers and exemplar companies will never finish. We have proposed future research into cache maintenance (specifically data eviction) across the semantic technology stack as a potential to solve the problems inherent with storing streaming data graphs indefinitely.

The DINT use case was successfully demonstrated to the scientific review board in an integrated framework displaying the results of several projects in an integrated user interface. The project correctly identified all changes in lines of business to the review board, running a comparison between an import stream and background data exemplar companies. In addition, we have partnered with Rensselaer Polytechnic Institute for additional team members. This project resulted in presentations and/or white papers at three conferences, and a manuscript is in progress for eventual submission to a peer-reviewed journal.

Signatures of Community and Change

Alan R. Chappell

This research aims to identify and validate a novel set of computationally tractable signatures for social media data that signal the presence of significant community events such as dissolution, schism, conflict periods, and ideological change.

A community is a set of individuals that interact in a shared environment around a set of shared interests, values, or problems. Historically, this shared environment has been a physical area, but it more recently includes a cyber or virtual space defined by a common communication fabric. Being made up of independent individuals also means that communities are dynamic in many ways. Community membership can change over time, member's interests and degree of participation in the shared environment can evolve, and the central pattern of shared interests and values can itself evolve. The advent of online social networks has dramatically increased the quantity and quality of the data available to study such communities, and many of the necessary computational tools have now been developed. PNNL has previously explored the use of behavior-based features as well as features extracted from message content as a way to identify abstract groups. However, the underlying models for understanding this data are typically rooted in topological approaches and static analysis. We still have a very limited understanding of how social media communities evolve over time, and because of this situation, we still do not have reliable signatures that indicate interesting points in a community's evolution.

This project addresses the above-noted technical gap, focusing on the intersection of two techniques: PNNL's work on computationally understanding the content of individual social media postings, and a new approach to modeling social network propagation effects pioneered by the University of Washington. Our overall objective is to use these techniques to identify and validate a novel set of computationally tractable signatures for social media data that signal the presence of significant community events such as dissolution, schism, conflict periods, and ideological change.

An important principle in analyzing general community behavior is that not all members are equal in their influence over other members. Certain members ("influencers") have superior knowledge, authority, or rhetorical skills around particular topics, and their contributions to the community carry more weight, propagate further, and more powerfully affect the contributions of others. Consequently, we focused our research on approaches for three aspects critical for understanding social network evolution: detection of topic of conversation, community, and influence.

A leader or influencer in one topic often is not a leader or influencer in another topic. Hence, any influencer-based algorithms for community dynamics must be sensitive to topic flows. Topic detection in text is a technical strength at PNNL; however, the textual style of social media presents many unique challenges. We applied the outcomes of other PNNL research to segment conversations based on broad topics to focus assessment on coherent communities.

Identification of communities in social media is a distinct research area and is not our area of focus. For our work, we selected a known algorithm (Louvain) based on its high-quality results and good computational characteristics. However, Louvain and other related algorithms require the user to identify connections between individuals prior to identifying communities. This situation is not possible for many classes of real social network data such as Twitter. Our team demonstrated several approaches to addressing this limitation, including the use of analyses based on transfer entropy and other information-theoretic concepts to infer connections based on observed network activity.

Several techniques have been developed to identify influencers in social media and online social networks. We collaborated closely with University of Washington researchers on the PHYSENSE system that they developed to analyze topic propagation in communities using physics-based algorithms derived from the analysis of fields. PHYSENSE can also be understood as a computational instantiation of a simple sociological model of influence propagation, giving it an independent plausibility. By adapting PHYSENSE to run on the PNNL Institutional Computing (PIC) system, we were able to validate previous results independently and assess computational requirements in the face of the large scales of social media. PIC also provided an effective mechanism to test the impact of multicore architectures on this performance. Building on the PHYSENSE system provides a sociologically grounded and computationally tractable approach to assessing influence in social media.

Ultimately, these three aspects – topic, community, and influence – form a set of features to build signatures that enable understanding community behavior. This research established baseline capabilities to quantify all these features. Further research using machine learning techniques over the features as they evolve may build on these results to identify specific signatures of community change.

PN14016/2600

Signatures of Illicit Nuclear Trafficking for Strategic Goods (SINTS)

Kirsten E. McNeil

This project identified, compared, and characterized procurement networks within large international commerce datasets to integrate data and knowledge from various domains and subject matter experts (SMEs). Our outcomes support expedited, reproducible, holistic foundations for nonproliferation analysts to examine countries and sensitive commodities and procure networks that connect them.

The international spread of sensitive nuclear technologies poses a serious threat to the nonproliferation community. Analysts addressing the challenge tend to focus on one of two problem spaces. First, they assess export control license applications for dual-use nuclear commodities for the validity of export, primarily through verification of the end-user of the commodity and its declared end use. Second, they examine a country's nuclear fuel cycle to determine the state's current and planned nuclear activities. However, the two analytical communities may work in isolation, which results in a lack of comprehensive understanding of the context of a commodity and company or country.

To provide some of the above context, this project used tools and mathematical methodology to automate the identification and characterization of procurement networks consisting of commodity and company pairs. While the ultimate goal is to apply the tools and methods to procurement networks of strategic nuclear goods, we focused on non-sensitive proxy case studies in the automotive and housewares industries to develop and improve our approaches for the transactions in which the context is known.

First, our team focused on understanding the procurement network and illicit nuclear trafficking problem spaces to define our analytical questions and approaches. The team conducted an extensive literature review covering illicit nuclear trafficking networks, proliferation financing, supply chain management, constraint based reasoning, and competitive intelligence. The team also conducted an SME survey regarding the export control license application process and state-level nonproliferation analysis captured in Bayesian network models by previous projects. Finally, team members engaged in job shadowing with PNNL analysts to understand their processes, data sources, and use of analytical tools. Expert elicitation and interviews were used to provide job performance context and details.

To analyze a procurement network, there must first be recognition that the network exists. In the current analytical workflow, analysts build networks manually as they encounter new information that link entities (individuals, companies, countries) with commodities (materials, equipment, finished goods). Analysts use their knowledge of companies, entities, or commodities to search databases for various spellings and abbreviations of names or addresses and develop these networks in an iterative fashion, which can be time consuming.

Once a network is identified, we want to explore its characteristics. Our team investigated two ways to comprehend a network: through similarity (to determine quantitatively how similar one network is to another) and anomalies (to understand normal patterns of behavior and attempt to determine what derivations from those patterns could indicate). For network similarity assessments, we used edit distance and sub-graph comparisons. Edit distance (modified for computational optimization) reflects the number of changes (additions or subtractions of graph nodes and edges) required to make one graph identical to a second graph. While edit distance does provide a telling story about the similarity of two networks, it is highly influenced by graph sizes. Additionally, we found that data biases such as geographic focal point could overwhelm any functional relationships between the two entities. We overcame these hurdles by creating a vertex cover that minimized these data biasing features and by comparing the data-based graphs with similar sized graphs of random data.

In FY 2014, we explored the anomalies within a network using detection algorithms to identify shipping records that appeared to be outside of the normal stream of commerce using a local outlier factor score, which attempts to recognize natural clusters within the data and those records that do not fall into any of these clusters. Unfortunately, the amount and quality of data (typos, misspellings, and potential deceptive declarations) made it impossible to identify either the clusters or outliers.

PN14029/2613

For FY 2015, we transitioned from exploratory data analysis to a constructive approach for network identification and characterization along the record, company, and network levels, which involved a data preprocessing step to clean the data noise found in 2014 studies and ensure proper comparison of the various data types. For the record level (transactional data between companies), a classifier was trained on one set of data and applied to a separate set (over 100,000 records). Our results showed that a classification tree using several different classifiers produces the best results with a very low error rate.

At the company level, we considered three metrics for describing a company's behavior: measure of business volume, economic role, and company motivation. The business volume is found by simply counting the number of imports and export from each year. The company's economic role was categorized as one of four roles: supplier, consumer, distributor and manufacturer. The challenge was to turn these economic concepts into mathematical constructs for a quantitative assessment. We defined what a "perfect" example of each role would be, such as the supplier exporting more goods that it imports, and the opposite case for a consumer company. A "perfect" distributor would import exactly the same number of commodities as they export. The definition of a manufacturer is more complicated, so the team defined what makes a commodity "more refined" than its constituent parts. A partially ordered set was created from the harmonized system (HS) tariff codes because they are structured to reflect commodity "refinedness" for some categories of commodities; for those that do not follow the scheme, the team developed an algorithm to map the elements of each category into a total preorder.

Moving up to network level signatures, the characteristics defined for each entity at the record and company levels are merged to reduce the noise level present in the graphs. For network level signatures, the team constructed a graph of all shipment data that informs the company role definition and identified subsets of entities that seem to be working together in a substantial way via community detection algorithms. These networks were compared using a PNNL-developed software GraphScape. When grouped into industry, the results showed fairly good agreement among the networks in the automotive industry. The housewares and appliance companies were not clustered according to industry as hoped, but given that several of the companies used to test the housewares definition (e.g., Sears) are also known to sell appliances, either grouping seems reasonable.

Finally, the team evaluated our algorithms' effectiveness in two ways: the usefulness to people already performing similar analyses and the ability to replicate the simple screening decisions that a human can make. To that end, we drew upon experimental design and expert elicitation techniques to create two separate studies. Results showed that analysts need to have confidence in the algorithm to rely on the data provided, they welcomed any visualization tools that might be applicable, and using structured entity relationship data to show how similar two entities might be would be useful. Additionally, when comparing our algorithms to human performance, we found that humans incorporate existing knowledge into their assessments – not surprising but difficult to quantify in an algorithm. The human subjects also took more data into account in some of their record similarity comparisons beyond what the algorithm was designed to do. Cluster analysis matched participant responses closely and may provide some advantage to an analyst. At the network comparison level, the results were similar for both parties, but differences arose at the point where the algorithm stopped ranking companies, yet these results are promising.

Streaming Data Characterization

Mark T. Greaves

We are creating an integrated resource of high speed, streaming data characterization and analysis algorithms upon which future projects can build.

Initial processing of streaming data sources is an area in which there is substantial previous work. We planned a set of related projects that will survey the scientific literature on initial stream processing algorithms for co-design domains, implementing the promising projects and tasks as well as evaluating their performance. We will use these studies to qualify potential university partners for their suitability within longer-term cooperative research and development relationships. There is currently no repository that gathers together the state-of-the-art in powerful online analytic algorithms that can process data on the fly. With this in mind, our repository will be not only critical for success but also a lasting resource for PNNL.

We directed four exploratory projects within different organizations, as described below.

Foundational streaming data preparation methods. This work was performed by Rensselaer Polytechnic Institute (RPI) and carried many initial research tasks, including a categorization, survey, and component listing for popular open-source and commercial off-the-shelf (COTS) streaming frameworks; an analysis of the specific uses of the selected frameworks that identified the overall strengths and any breakthroughs in these frameworks; and a new formal ontological classification of the chosen frameworks based on the technical approach.

Visualization of hypotheses about streaming data. This work was performed by the University of Utah's Scientific Computing and Imaging (SCI) Institute and addressed statistical hypothesis testing as a visual tool for quantifying and understanding complex phenomena. An approach was developed that relied on simultaneously leveraging the analytic capabilities of both humans and computers using visualization as a knowledge-sharing interface between the two. For example, computers are good at extracting linear models, dealing in high dimensional spaces, and processing large quantities of data. On the other hand, humans tend to be much better at more abstract tasks, such as identifying nonlinear models and classifying data. In this work, the human helped to build the computer model, while the computer simultaneously helped the user to build the mental model of the data that resulted in a prototype.

Data summarization for streaming scientific video. At the University of Washington, this project supported initial architectural work to address the significantly growing scale of microscopy video data. The scale of imagery coming from new systems such as PNNL's dynamic transmission electron microscope requires developing new streaming algorithms even for common tasks such as retrieval, interactive browsing, or compressing video content. This project developed architectures and basic summarization algorithms to identify pertinent scientific content from sequential imagery on the fly and produce a condensed version of video as an output. The techniques also meet single-pass and high throughput requirements.

Event summarization in microscopy imagery. At the SCI Institute, we collaborated with biologists that had streaming image analysis needs. For two selected bioimagery problems, we determined the best set of nonstreaming algorithms and proposed modifications to methods to adapt them for streaming image analysis in experimental settings. Expected impacts include techniques for automated analysis of image data from microscopes to drive experimental techniques as well as the development of new techniques for quickly post processing acquired image data.

In FY 2015, we expanded and formalized our collaboration with university partner RPI. Together, we focused on studying specific symbolic techniques to consume and reason over a volatile data stream. The project leveraged selected COTS and open source components of the Semantic Web software stack and explored the interaction of these different software frameworks on choices for streaming data models. Along with RPI interns on site at PNNL, we commenced work on developing a library of algorithms to manage optimally a cache for symbolic data. This new family of algorithms allows us to account for the interaction between the particular symbolic knowledge representation formalism (e.g., description logics of various expressive powers), the different reasoning engines provided by the Semantic Web software stack, and the parameters of the streaming analysis task.

This project has yielded four conference papers, and we anticipate that the RPI relationship will carry into FY 2016.

PN14076/2660

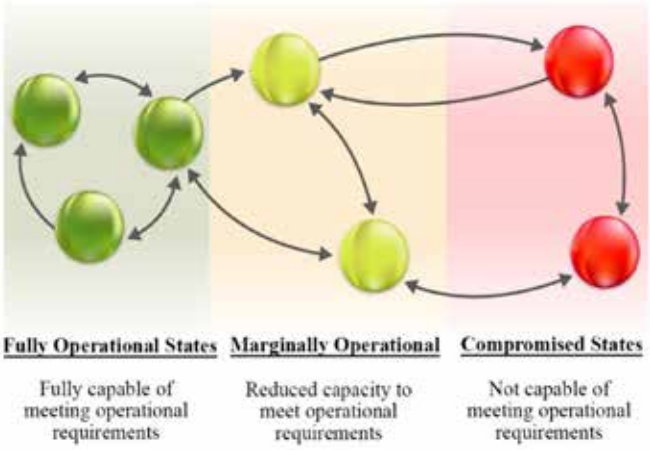
Theory of Resilience

Pradeep Ramuhalli

We are developing and evaluating a theoretical framework for resilience to provide the technical basis for evaluating cyber defense and reconstitution approaches.

Resilient cyber systems ensure that an organization's mission critical functions continue to operate in the face of ongoing detrimental events. Assuring resilience requires techniques for robust design, evaluating proposed solutions, and identifying optimal solutions to dynamic reconstitution of compromised cyber systems. The reconstitution response, including recovery and evolution, may require significant reconfiguration at all levels to render the cyber system resilient to ongoing and future attacks or faults while maintaining operating continuity.

The quest for resilient cyber systems has seen a number of technical approaches (such as moving target defense) that add specific properties such as diversity, redundancy, deception, segmentation, and unpredictability to make the system more resilient to attack vectors. However, these methods cannot be applied readily after a system has been compromised. It is also difficult to ascertain whether such tactics are applicable under any attack scenario or if limitations exist. The objective of this research is to develop and evaluate a theoretical framework for resilience that identifies specific principles of resilience that may be applicable to cyber systems; include a mathematical methodology that relates these principles to elements of a cyber system, and integrate decision making into the framework so that decisions in a compromised environment may be made with the goal of achieving continuity of operations in a fast, cost-effective manner.



Conceptual representation of reconstitution in cyber systems, moving the system from one of several compromised states to a fully operational state.

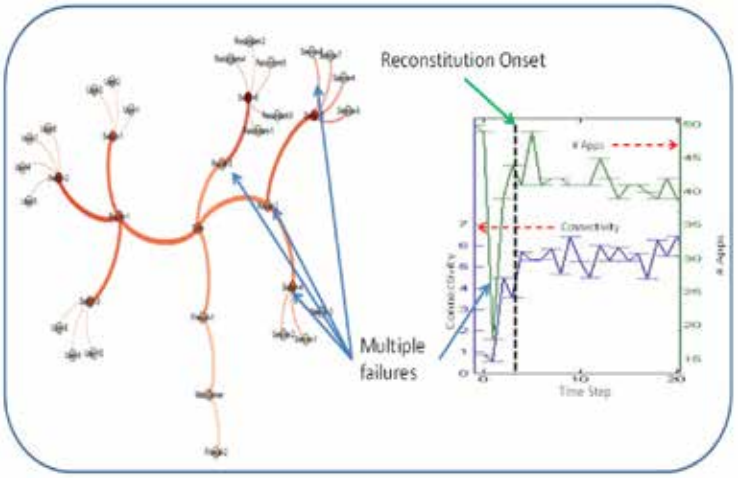
The resulting framework will enable the identification of key components of resilient cyber systems; decision making with uncertain information (i.e., the design and recovery decision-making methodologies may need to function with limited information); and asymmetric advantage (increased cost to the adversary should be a factor in the decision making). The results of this research will also provide insights into measurement needs and success criteria for asymmetric resilient cyber infrastructure. Current frameworks for resilience encompass four basic concepts that collectively enable robust design (anticipate, withstand) and dynamic reconstitution (recover, evolve). In FY 2013, a theoretical framework for dynamic reconstitution that applied principles of multi-objective optimization was developed and evaluated. For FY 2014, the technical development focus was on a theoretical framework for cyber resilience that included reconstitution.

During FY 2015, the theoretical framework from the previous year was refined and evaluated using simple scenarios. We used a state-space formulation to characterizing resilience in the face of impediments. Cyber system states included mission-relevant variables (such as system configuration) and were used to describe model(s) that captured dynamic system behavior. A mathematically rigorous definition of resilience in this context is the degree of system stability at or near its operational state, defining conditions on system dynamics, connectivity, and control input locations. The problems of robust system design and reconstitution may be defined in terms of a multi-objective optimization problem with resilience as the optimization function of interest, and resulting solutions may provide insights into tradeoffs between resilience, cost, risk, and other relevant metrics.

Challenges in this context included defining a cyber system state in a manner relevant to the mission, identifying relevant operational states that support the mission, and developing methods for reconstituting compromised cyber systems. We previously defined state C_t of a cyber system at time *t* as a representation of its key properties; this could include configuration information directly or be the result of mapping configuration to a metric of availability, integrity, or confidentiality. We assumed the existence of a well-defined notion of mission and performance measures. The theory of resilience was evaluated using several abstractions of cyber

PN13063/2544

systems, including queues and small (30–40 node) graphs. Queueing models represent systems that store and process requests from other entities (such as clients), and key properties include queue length, resource limits for processors, and number of queues. At a different level of abstraction, an *n*-node system with *m* critical services is described by a graph G that captures the connectivity structure of the cyber system at one or more layers (network, services, data, etc.) in the system stack. Here, a node represents some computational resource, such as a computer or a server that can run any subset of the *m* services.



Example of simulation results. The system connectivity map (left) at time 0 shows a failure of multiple nodes due to some event that negatively impacts metrics measuring connectivity and continuity of operations (right). When applied after the failure, reconstitution methodology helps the network recover while improving the continuity of operations.

Simulation studies consisted of disrupting the system either by limiting availability of mission-critical components or reducing the integrity of critical systems (which may also limit availability) and evaluating the ability of the system to maintain mission as a function of the state variables. Results to date indicate viability of the theory of resilience; specifically, resilience as a system attribute related to controllability, observability, and stability appears to be reasonable and may be applied in a multi-objective optimization approach to determine system states that continue to meet mission needs.

Results of simulation studies also indicated that the multi-objective optimization approach may be viable for the reconstitution of compromised cyber systems. Based on simulation results, the approach was capable of reconstituting systems and improving overall resilience in the presence of serial disruptions (i.e., as the system is recovering, a subsequent disruption occurs); however, the recovery may be somewhat slower, as the approach needs to account for severe reductions in capacity. The formulation also provides a mechanism for evaluating performance of other approaches to a reconstitution of compromised cyber systems. This formulation and results are documented in a journal paper submitted in FY 2015.

Future plans include transitioning the theoretical concepts to integrated demonstrations that evaluate and quantify the performance of technologies for resilience.

Topological Analysis of Graphs in Cyber Security (TAGs-CS)

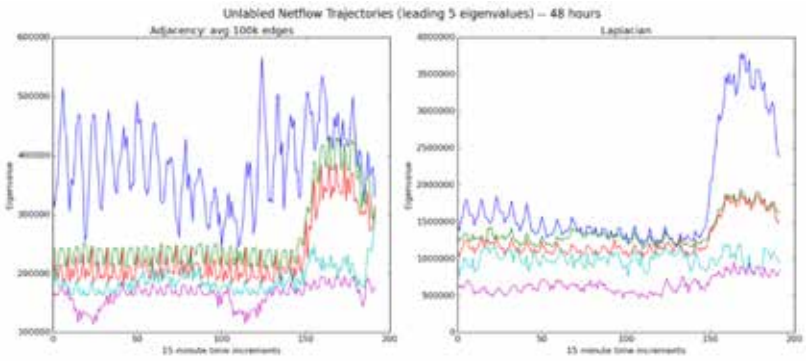
Emilie A. Hogan

We are discovering shapes, structures, and overall cyber system behavior using topological data analysis of graphs derived from data, providing analysts with information to determine the state of their cyber system.

Topological methods have been deployed in real-world problem domains with great success (e.g., signal processing, medical imaging, and drug discovery). These methods were created to identify the largest, most robust shapes and structures in data sets and to discover average system behaviors. In cyber systems, the network is as dynamic as elements (e.g., computers, printers, and mobile devices) sign on and off, as communications begin and end, and when interactions with other networks initialize and complete. In this project, we analyze these dynamic systems using topological methods that can lead to new tools for system administrators to judge resiliency and ensure that missions can still be completed.

We hypothesize that this analysis will provide a way to differentiate between resilient and non-resilient system states, possibly even identifying different causes of non-resilient states. Within the broad theory of topological data analysis, we are using two major techniques, both coupled with novel statistical graph analysis. The first technique, persistence, is for discovering most prevalent underlying higher order structures of a system. We track these structures as the system evolves through time. Dynamic graphs representing system processes will be tracked. We hypothesize that finding times when certain structures persist could indicate periods of network resilience, whereas degradation or loss of these features may be periods in which resilience is lost.

Our second technique is tracking dynamic graph evolution through dimension-reduced graphic representations. We reduce a graph to a small vector of statistical measurements and use these values as a proxy for the graph. We then track how graphs evolve through a low-dimensional visualization using machine classification to learn patterns of different behavior types. Both techniques, along with statistical analysis of the dynamic graphs, are run side-by-side to correlate results.



The evolution of five eigenvalues in five different curves for the adjacency (left) and Laplacian (right) matrix.

In FY 2015, we identified useful data sets on which to test our methods. Internal remote desktop protocol (RDP) sessions merged with NetFlow records became our target data set. We collected and performed exploratory data analysis before using topological methods. In addition, we identified external sources of simulated NetFlow with attacks on which we tested our methods. Within our two major analysis methods, persistence and dimension reduction, we have working prototype capabilities against different data sources. In persistence, we used one of our sources of simulated NetFlow and produced anomaly scores over time based on topological persistence of a derived distribution function. The distribution measures the probability for a single vertex to receive a packet at a given time point. Our analysis resulted in the detection of several periods of anomalous traffic at a single IP address, each lasting approximately 30 min, known to have been the victim of distributed denial of service attacks lasting 30 min. Though the times of these attacks are unknown, we hypothesize that they coincided with the anomalous events discovered by our methods.

Our dimension reduction capability was tested against our internal NetFlow data source. A period of 48 hours beginning around 5pm on Saturday has been partitioned into 60-min periods with a 45-min overlap. Each of these hour-long data sets is shown graphically, in which vertices are IP addresses and an edge represents a NetFlow record between two IP addresses. The spectrum of the adjacency and Laplacian matrices was calculated and the top five eigenvalues recorded, as shown in the figure. We see relatively stable behavior on Saturday and Sunday evening, followed by a ramp up on Monday morning, and a decrease on Monday afternoon.

Our FY 2016 activities will focus on exploring these and similar methods, further and implementing them in a more general case beyond their current data source. Our overarching goal is to explore algorithms for use by cyber analysts to detect change of state in cyber systems.

PN14086/2670

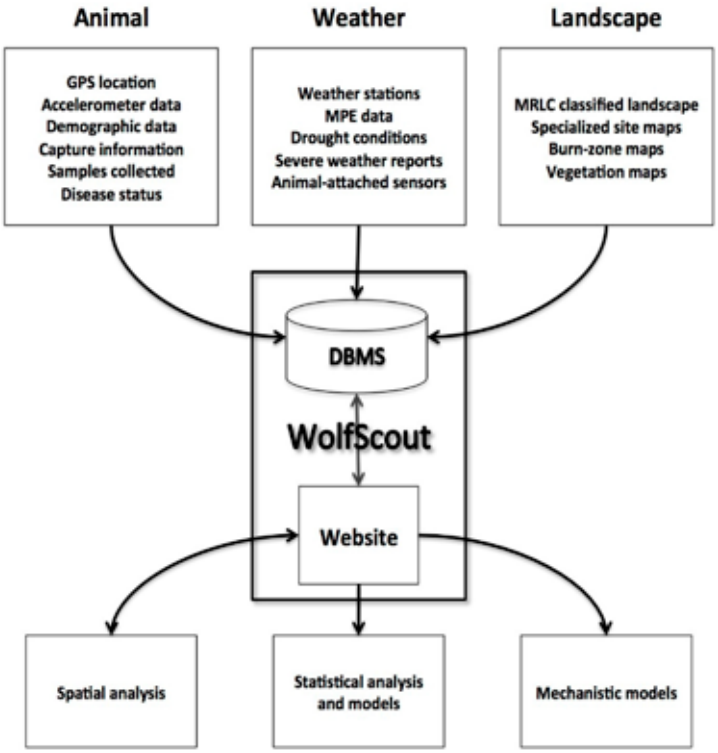
Towards One Health Disease Surveillance

Courtney D. Corley

The information derived from this study increases our understanding about human-wildlife encounters and environmental factors that may elevate the potential for zoonotic disease transmission events.

Wildlife ecologists strive to model and predict correctly the complex relationship between animals and their environment. This information helps to facilitate management decisions about the delicate ecosystems that impact public policy and health. Through rigorous research findings linked across multiple disciplines, an understanding of the dynamics between environmental factors (e.g., weather, drought, and landscape) and animal movements or behavior can drive management decisions regarding the conservation of land, species, and the spread of infectious diseases.

A breadth of detailed information is collected daily about biotic and abiotic elements in diverse ecosystems. Understanding the relationship between these elements within any given ecosystem is paramount in order for wildlife research to advance. Further, questions concerning the impact of the environment, including climate change and anthropogenic factors about movements, resource selections, and disease cycles of these animals, introduces additional complexity and data that all need to be processed together. The capability of integrating heterogeneous data in a standardized manner is lacking but is essential for efficiently processing the enormous amounts of information available to address these higher level questions that span multiple disciplines.



Outline of the WolfScout database management components and approach

By using a database management approach to pursue this type of interdisciplinary research, our resulting product from this project will promote the interoperability in data between researchers and software applications while standardizing the analyses of animal interactions with their environment. Ultimately, this design should allow for more complex questions to be addressed in a rapid, reliable, and repeatable manner to aid in management decisions based on scientific research.

This project involved the development of a prototype data management system called the WolfScout wildlife and weather integration system to address questions of how current environmental conditions affect animal movements and interactions with their surroundings. The web-based system automates the integration of the latest technological advances in wildlife GPS collars with the closest weather stations, point-location drought conditions, and severe weather reports, along with animal demographic information. With a spatial database management system (DBMS) at its core, WolfScout provides users with the ability to calculate the spatial interaction distances between animals and either classified landscape data or other animals.

As an example of how the relationship between weather and wildlife movements can impact public health management and response, mesocarnivore submissions for rabies testing in various counties throughout the state of North Carolina were used to evaluate whether weather conditions or events correlated to wildlife interactions with people and other animals. Through this research, we were able to identify various weather variables that potentially affected aggressive animal behavior toward either humans or domestic or agricultural animals.

PN15038/2713

Unmask Signatures of Cell Perturbation Hidden in the Normal Variability Between Cells

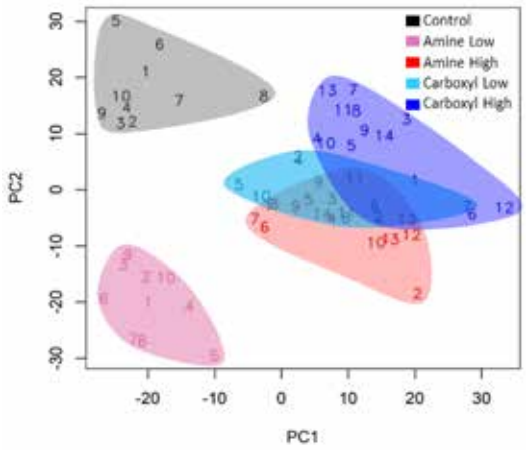
Galya Orr

The new analytical approaches developed under this project will be applied to answer relevant research questions where insights into the functions of individual cells are required.

Cell population measurements provide averaged values often dominated by the most robust or abundant processes, where molecular details and variability between cells are buried in the averaged measurements. Analysis techniques such as single cell transcriptomic analysis have the potential to unmask cellular heterogeneities and, for example, identify a cancer cell among healthy cells in a tissue or a cell with a critical function in complex microbial communities. Specifically, single cell RNA-Seq is a young field, with the first publication appearing in 2009 and remains largely missing statistical tools for detecting unique signatures of individual cells that may be buried in the natural noise created by the normal variability between cells.

We are establishing new tools to identify signatures of cell abnormality or responses to perturbation that may be buried in the natural noise created by the normal variability between cells. These tools could be also applied to decipher the role of individual microbial cells in complex microbial communities to understand their function in C cycling, biomass degradation, plant resistance, or the release of volatile organic compounds. Specifically, we have focused on single cell RNA-Seq datasets for cells perturbed by engineered nanoparticles (NPs). The exploding growth in the use of nanomaterials in a wide range of applications is expected to increase both the intended and unintended human exposure to NPs, but a great deal of confusion exists about the properties that make a NP toxic or biocompatible. Distinct physical and chemical properties of the NP engage and activate distinct proteins and cellular pathways that in turn govern the fate of the NP and its impact on the cell and, ultimately, on human health.

The relationships between NP properties and key cellular processes and response are far from being understood. This knowledge gap is largely due to experimental challenges that NPs present, including the difficulty to achieve uniform NP distribution over the exposed cells. The distribution typically spans 2 to 3 orders of magnitude, indicating that some cells are "overloaded" with hundreds or thousands of NPs, while other cells are loaded with only few or no NPs. Responses such as regulation of gene expression or pathways have always been measured in the population as a whole. This approach identifies averaged, often most common or generic processes, while leaving other critical processes undetected due to the dilution of signals across many cells, each caries a different number of NPs. As a result, it is unclear whether population studies identify only generic, emergency state responses in a subset of "overloaded" cells, and whether responses unique to the properties of the NPs at lower load levels, where many cells might carry not even one NP, are diluted and missed altogether. To answer these questions, we exposed alveolar epithelial cells, which present a vulnerable target to airborne NP exposure and sorted individual cells by their NP load for single-cell RNA-Seq analysis. Using these datasets, we have been developing analytical tools to enable the detection of unique response signatures in these datasets.



The first two principal components for the normalized gene expression counts of the top 100 genes, selected using classification trees by their effectiveness to separate treatment groups. Each single cell data for each treatment group is numbered and color coded.

Quantum dots (QDs) have been generating interest in a growing range of applications from solar and interfacial charge transfer, including photovoltaics and solid-state LED lighting to biological research, drug delivery, and medical diagnostics. However, controversy still exists about the type of coating and functional groups that could make these promising NPs biocompatible. By developing new approaches to analyze single cell RNA-Seq data of cells carrying lower or higher loads of animated or carboxylated QDs, we have begun to uncover unique response patterns to distinct QD types. Using classification trees recursively, we identified the top 100 genes that contributed the most to the separation between the treatment groups. We found that these top 100 genes could more effectively segregate cells by their treatment groups than all 9233 genes found in all the single cell RNA-Seq datasets. This separation is demonstrated by the principal component analysis (PCA) shown in the image.

PN15102/2777

User-centric Hypothesis Definition

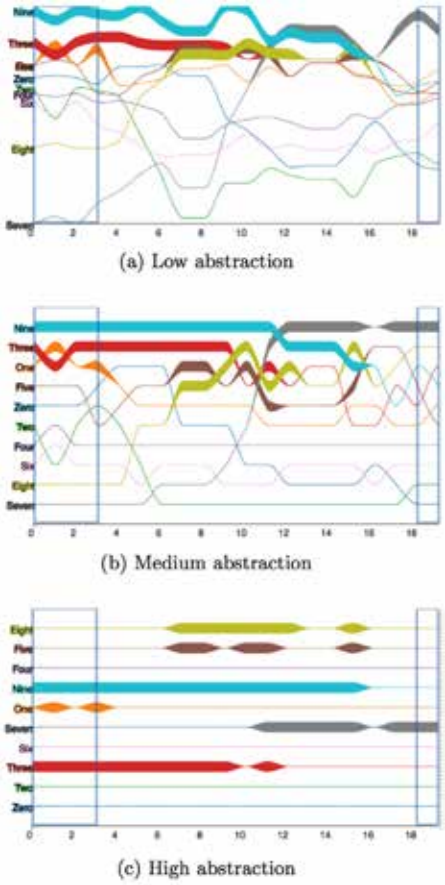
Dustin L. Arendt

Our research aims to reveal effective techniques for visual communication of machine learning output to non-expert users in a streaming environment.

The rate of adoption of machine learning and analytics is rapidly outpacing the comparatively small group of expert users who understand the technology. While there are many visualization tools and techniques to support data scientists, software engineers, and statisticians who produce sophisticated machine learning models, there is relatively little support for the typical "naïve user" who consumes these models. These tools, which generally aid with high dimensional data exploration, feature selection, and parameter fitting, are well suited toward post hoc analyses in a forensic setting with an expert user. However, these tools are not appropriate in a deployed space where decisions are required in real-time from analysts who we assume wish to leverage sophisticated analytics without comprehending the underlying algorithms.

Our research goal is to gain insight on how to support analysts through visual communication who want to leverage machine learning analytics to understand a complex changing system. As visualization researchers, we achieve this goal by designing visualizations for a use case and evaluating the effectiveness of our techniques in a controlled human subjects experiment.

Our hypothesis is that the level of abstraction of the visual communication has a strong influence on the user's ability to accomplish tasks related to streaming analytics. Specifically, we believe in the fairly counter-intuitive assertion that "less is more:" showing less detailed information in a more abstract, possibly loss-filled manner can actually improve the user's speed, accuracy, and confidence. We are testing this hypothesis by running a controlled experiment in which we measure visualizations of the same data with varying levels of abstraction across two tasks related to streaming analytics: change detection and change explanation. One of the challenges in designing an experiment of this nature is controlling for the desired effect want (e.g., level of abstraction) while keeping other aspects constant (e.g., visual encoding). We succeeded in developing three visualizations suitable for communicating streaming machine analytics with three different levels of abstraction but using the same visual representation.



(a) Low abstraction

(b) Medium abstraction

(c) High abstraction

This figure illustrates how we vary the level of abstraction while keeping other aspects of the visualization such as visual encoding constant. In each visualization, streaming output of a binary classification model is represented by a line, which is thick when the model's confidence in a positive classification is high. In (a), the least abstract visualization, the mode's confidence is directly encoded on the vertical axis. In (b), the relative ranking of each model is encoded on the vertical axis. In (c), the most abstract visualization, no data are encoded on the vertical axis, and models are ordered alphabetically.

Other challenges we faced included determining how to make our results repeatable and generalizable to the wider population beyond participants in our experiment. Specifically, there is a lack of open-source datasets suitable for evaluating streaming machine analytics. We approached this problem by developing a technique for generating streaming data from an existing static labeled multivariate dataset, of which there are hundreds of open-source examples. We used a clustering algorithm to down sample the dataset, which helps to reduce over fitting in the model. We simulated "class drift" in the data stream by using a biased graph random walk. Ultimately, we measure the user's ability to detect and explain this drift using the visualizations that we designed.

Work for FY 2016 will include completion of our experiment, which entails data collection, analysis, and the publication of results. Following these activities, we will focus on semantic interaction techniques for streaming machine analytics in which changes to the underlying machine learning model (including parameters and weights) are inferred from user interactions with visualization. We intend to develop and evaluate this semantic interaction methodology using the visualizations already developed for single streams and new visualization techniques based on storylines for multiple concurrent streams.

PN15025/2700

Visual Analytics Platform for Large-scale Hierarchical Control System Data

George Chin Jr.

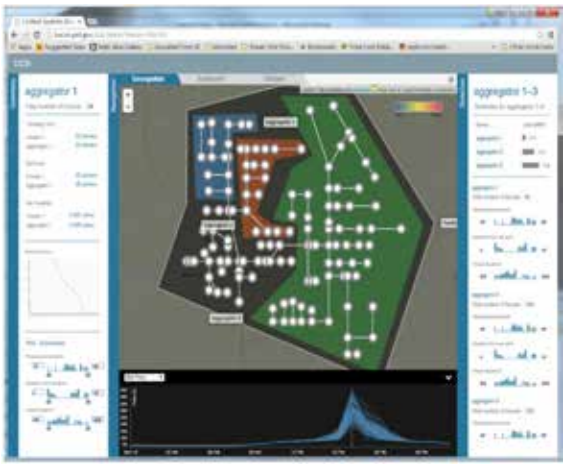
To enable control system designers to develop and evaluate modern-day control systems more effectively, advanced visual analytics capabilities may be developed and deployed to allow designers to better explore, interpret, and analyze the behavior of complex systems and the data and results they generate.

Infrastructure systems today are generating ever-increasing amounts of data that are highly complex, relate to large numbers of sensing and/or control end points, and involve in multiple scales of operation. Innovative and advanced visualization tools and platforms are needed to enable control system designers to

- test and refine their control systems
- access, visualize, evaluate, and compare results at multiple levels of detail and aggregation
- understand how controls impact, and integrate and interact with agents and systems.

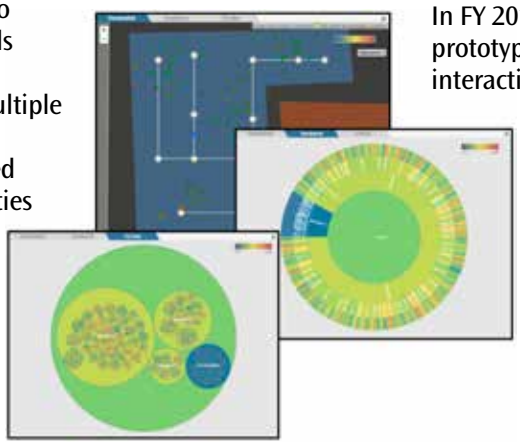
We are focused on researching and developing novel visualization techniques and tools for navigating and exploring large-scale, massive-entities control system data. Tools will feature intuitive visual representations, zoomable interfaces, multi-scale layout and navigation, and scalable performance. In addition, the project is developing a visual analytics platform to manage and integrate visualization tools with complex models and data that will combine and examine results across multiple experiments. This platform will provide connections to data sources, coordinated views of data and models, and capabilities to search, filter, and integrate complex control system data.

In FY 2015, we worked closely with control theory to gather their visualization requirements, specifically distributed control and mechanism design projects associated with the internal integrated demonstration. For both projects, derived visualization requirements centered on comparing the results of the new control systems against theoretical or competing systems and evaluating the effects on the entities and end-points they control. To address these visualization requirements, we developed a visual analytics prototype that allows system designers to examine control system behavior and compare experimental results using time plots. The user may select a particular time point or interval to access and display higher resolution views of controlled entities and/or end-points, including their states. Three different visualization techniques (geospatial view, sunburst, and packed circles) were developed to show end-point results from different logical perspectives (geospatially, hierarchically, and within clusters).



Interactive visual analytics environment for data exploration of control system experimental results.

Currently, the project is evaluating the usefulness and usability of the visualization prototype against experimental results generated from the integrated demonstration. In this effort, control system designers perform the same analysis process to examine and validate their systems but use the visual analytics platform to carry out the analysis. We then evaluate whether the analysis was more effective using the visual analytics platform compared to the original analysis approach.



Geospatial, sunburst, and packed circle visualizations are used to highlight visual patterns, along specific perspectives such as geospatial, hierarchical, and clusters.

In FY 2016, we will extend the visual analytics prototype to enable a more efficient and facile interaction with control system parameters and results. We will investigate and prototype an interactive control system visualization to show dynamic control, communications, and behavior among system entities. As network simulations progress, the control system visualization may be enhanced to highlight network conditions and effects. Finally, we will integrate and link the control system visualization to other information visualization techniques to enable visual data mining and analysis.

PN15003/2678

Nuclear Science and Engineering

An *In situ* Investigation of Gamma-AlOOH Dissolution under High pH Conditions

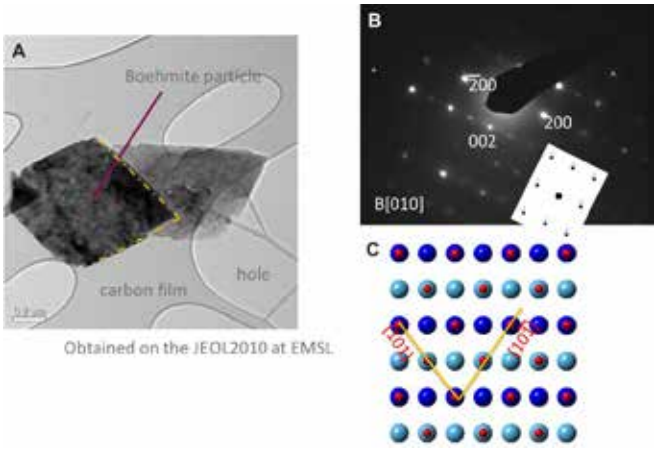
Edgar C. Buck

The results of this project will help lead to a new understanding of the dissolution processes, allowing us to test the role of intrinsic and extrinsic factors on the variability of mineral reactivity.

Reactions at solid or particle surfaces include dissolution, precipitation, and sorption. Heterogeneities of the mineral surface that include defects, dislocations, and expression of different crystallographic faces represent intrinsic factors that cause variability in reactivity. Extrinsic factors that may affect reactivity include sorbed molecules and colloids, tenacious nanoscale surface coatings and, particularly relevant to nuclear system, nano-bubbles from radiolytic processes. This project is probing dissolution processes relevant to Hanford waste processing and spent fuel dissolution at the nanoscale with modern *in situ* electron microscopy techniques and examining the influence of intrinsic and extrinsic factors on the variability of mineral reactivity. Our intent is to develop procedures and capabilities for flowing solutions (caustic solutions), adding soluble alumina and various colloidal particles (e.g., iron, chromium, manganese, and titanium oxides), and running the system at above-ambient temperatures. Though it is not yet possible to duplicate the conditions expected in the Hanford Tank Waste Treatment and Immobilization Plant (WTP; e.g., temperatures >80°C and highly caustic solutions), we are observing the process at the microscale and obtaining the rates of reaction directly that could be input into the models (such as the AlOOH-shrinking particle) and also for new computational approaches being developed by others, including phase field modeling.

The dissolution and precipitation of gibbsite [α-Al(OH)$_3$] and boehmite [γ-AlOOH] is of prime importance to the final disposition of high level waste (HLW) stored at the Hanford Site. The high aluminum content in the Hanford tank waste stream is incompatible with current durable glass formulations and needs to be minimized before vitrification. The aluminum oxide that formed from the precipitation of waste streams from plutonium weapons processing is present as colloidal-sized particles in a highly alkaline and high ionic strength solution. Although high radioactivity is a significant challenge to waste processing, the influence of radioactivity on the behavior of the aluminum phases and their subsequent processing is unknown. Common in the tanks, gibbsite and sodium aluminate are easily dissolved by heating under caustic conditions; however, boehmite is more stable and requires more aggressive conditions.

FY 2015 investigations focused on boehmite synthesis to produce the characteristic platy phases that have been observed in the Hanford tanks. Initial synthesis tests resulted in the formation of pseudo-boehmite, which was examined using several different microscopes. Preparations were also made in the presence to Cr, Fe, and Mn. The image shows an example TEM analysis of a large platy boehmite that was produced synthetically. Although such phases will be useful in the study, they are too large for *in situ* TEM analysis but are reasonable for the *in situ* scanning electron microscopy (SEM) imaging. The pseudo-boehmite produced initially was also examined in solution under *in situ* conditions and *ex situ*.



Transmission electron microscopy (TEM) analysis of boehmite platy crystals: A) image of particles; B) selected area electron diffraction pattern taken along the B[010] zone axis; and C) atomic model of [010] surface.

As a component of the intrinsic effects on boehmite reactivity, we focused on understanding how impurities may be incorporated into bulk Al-oxy-hydroxide phases. It is unknown whether a Cr-enriched edge reduces the reactivity, but we will address this area of study in FY 2016. Simulation of incorporation or association behavior is being considered from two different modeling perspectives, the cluster and the bulk approach. We need to determine how

PN15090/2765

solution species interact with Al-oxy-hydroxide substrates and how the chemistry/electronic structure affects interaction with adsorbates. Because there are strong parallels between Al- and Fe-oxy-hydroxide systems, we are using the wealth of knowledge on Fe-oxy to understand how chemistry and electronic structure affect the dissolution behavior of boehmite and related phases. In support of the experiments, incorporation energies (E_{inc}) can be calculated as a function of Cr(III) depth in boehmite surface slabs to determine if it (and other impurities) will most likely partition to surfaces or edges or incorporate into the bulk. Atomic resolution imaging, which was partially successful this year, will be attempted in FY 2016 on various specimens to look at bulk incorporation.

Also during FY 2015, we concentrated on both SEM and TEM imaging of the phase in solution. When performing dissolution reactions, there are several issues that make the *in situ* studies unique and challenging: relatively high temperature, very high pH, and high radiation fields. In particular, the WTP baseline caustic leaching process (pH=~13) was developed to operate at 85°C with a residence time of ~8 hours. Whereas such conditions are considered benign for engineering environments, they are extreme for current *in situ* cells.

An important aspect of this research in FY 2016 will be to develop dedicated holders for conducting experiments under more extreme conditions. In this regard, we initiated conversations with companies in the *in situ* microscopy field to develop cells that can be used under this harsh condition. In the immediate term, observations will be made under more benign conditions with appropriate simulants. Although we anticipate lower overall reactivity, observations at the micro- and atomic-scale should enable measurements and extrapolations. Ultimately, it will be important to mimic WTP operations. In following years, we will purchase or fabricate dedicated holders that will allow us to examine such rigorous conditions more characteristic of WTP as well as actual tank waste material.

Atomic Mass Separation for Enhanced Radiation Detection Measurements

Gregory C. Eiden

This project seeks to improve dramatically the measurement and detection of radionuclides of interest in the nuclear fuel cycle.

Sensitive measurement of radionuclides requires both high fidelity chemical separations of the isotopes of interest from the sample matrix and state-of-the-art detection of the isotope in the separated sample. Prior to this project, chemical separation was the only option for sample preparation. This research seeks to develop separations based on radionuclide atomic mass. With modern mass spectrometers (MS), such separations can be many orders of magnitude more effective than chemical separations. Our novel approach is expected to create a paradigm shift in the way radiochemical separations are thought about by experts in the field. The technique we are developing will lead to improved methods in fixed laboratories, but also in field deployed instrumentation especially for nuclear accident and terrorist incident response.

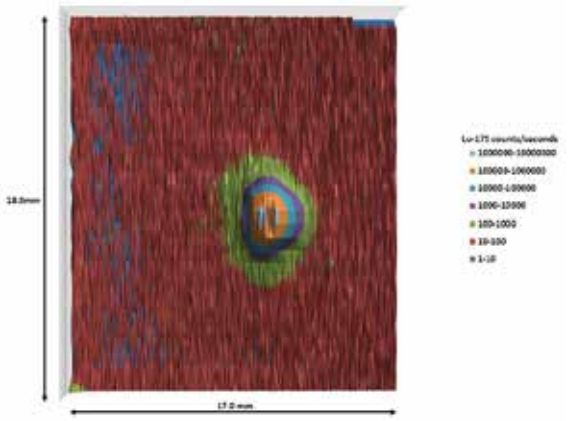
We developed a prototype instrument, preliminary method and demonstrated the ability to capture single mass (1 atomic mass unit) ion beams efficiently from an MS-based separator. Our objective is to explore the analytical performance of the prototype instrument, develop follow-on modifications, and obtain proof-of-concept data for key alpha, beta and gamma emitting isotopes. Our focus is developing instrumentation and methods for use in fixed laboratory analysis of radioactive environmental samples associated with fission and activation products from reactors (reactor accidents or routine releases) and terrorist use of a nuclear device.

In FY 2013, we developed a prototype instrument with which individual atomic masses could be implanted into a solid target, thereby enabling isotopes of a given atomic mass to be characterized radiometrically. The instrument is a modified quadrupole mass filter based inductively coupled plasma MS (ICP-MS). Preliminary tests and implant were characterized using stable isotopes. For FY 2014, MS-RAD was applied to a ^{244}Pu standard, creating a mass 238 implant and demonstrating the removal of all plutonium isotopes and ^{241}Am by alpha spectroscopy. The implant demonstrated at least 2 orders of magnitude enhancement of the ^{238}Pu, far below expectations. The limitation was an artifact of the radiation detection equipment.

During FY 2015, MS-RAD was applied to a sample of ^{137}Cs that contained a small amount of ^{134}Cs. The result demonstrated isotope separation of the same elements with above 4 orders of magnitude separation. The technique was also applied to the isotopic purification of nominally enriched isotope standards. The presence of other plutonium isotopes in the SRM limits the amount of material that can be used as a chemical tracer/spike in isotope dilution MS, thereby limiting the analysis. An MS RAD implant of mass 244 produced ~0.25 ng of >99.996% pure ^{244}Pu. A metallic substrate is the not the ideal choice if the implanted isotope will be recovered. Typically, isotope recovery involves a step of leaching or dissolution usually in acidic matrix that either etches or dissolves the implant substrate. The resulting solution may then contain contamination from the substrate, and isolation of the implanted isotope from the copper requires added chemistry.

A robust alternative explored in this research used an electrically conductive plastic sheet. An additional benefit of this material is that it can be pre-leached prior to implantation to remove contamination even from relatively high abundance elements like the alkali, alkaline earth and transition metals. The MS-RAD technique was used with several different elements on carbon doped polythene substrate. The isotope recovery appear excellent (>95%), with simple leaching that takes only minutes.

A single collector high resolution ICP-MS, the Attom (Wrexham, England) brought a new capability to MS-RAD experiments. The Attom operates at higher ion energies; therefore, larger mass selected ion currents could be attained, suggesting that one of these instruments could produce a purified isotope at a 10–20 times higher rate. Preliminary experiments produced implants with 99.99% of the isotope in 3–4 mm diameter spot. The image shows the first implant using ^{175}Lu conducted on the Attom. No yield experiments were performed, but the magnitude of the implanted ion response observed during imaging suggests possible ion loss during implantation, likely as a result of self-sputtering by the incoming high energy ion beam.



A LA-ICP-MS image of the first Attom implant for 175Lu.

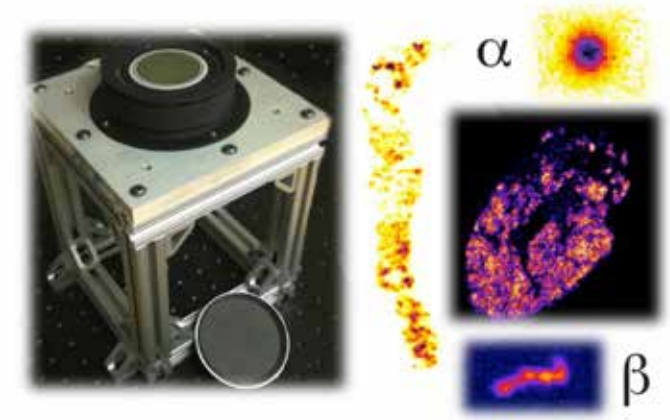
PN13015/2496

BazookaSPECT Neutron Imager

Brian W. Miller

This project is developing a high-resolution ionizing radiation imaging detector technology for specialized use in medical imaging, nuclear science, and national security applications.

During the last several years, BazookaSPECT, a new class of gamma-ray detector, 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 been employed primarily in pre-clinical medical imaging applications such as single-photon emission computed tomography (SPECT), which monitors level of biological activity (instead of just taking a picture) in a 3D region of anatomical structures. We are interested in exploring and characterizing the use of BazookaSPECT 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.



The PNNL iQID detector, images of alpha and beta particle interactions, and selected alpha-particle autoradiographs of tissue sections.

Our objective in this project is to establish a detector capability at PNNL and investigate, demonstrate, characterize, and improve the detection response to ionizing radiation. We are building a high-resolution position-sensitive neutron detector (~100 µm resolution, 10–16 cm diameter) that will be used in a variety of imaging experiments such as neutron radiography, diffraction, and neutron-coded aperture imaging. In addition, we will seek to develop applications that are enabled or improved upon by the technology. After establishing the capability, we aim to expand BazookaSPECT in terms of hardware, software, and applications.

As noted above, our focus was evaluating the response of the detector to other forms of ionizing radiation, including fission fragments as well as alpha, neutron, and beta particles. Results have been successful and, as a result, the detector has been renamed the ionizing-radiation Quantum Imaging Detector (iQID) to represent its broad response to ionizing radiation.

During FY 2015, we focused on developing and implement microdosimetry methods in which the dose (amount of grays) to a small clusters of cells is estimated. This activity involved the simultaneous imaging of a continuous region of tissue sections, where the total thickness spanned the range of the alpha particles. The estimated dose rate from these data can now be used to estimate the total absorbed dose using biopsy samples at different time points.

In addition to continued collaborations with Fred Hutchinson Cancer Research Center (FHCRC), the U.S. Transuranium and Uranium Registries (USTUR), and Mainz University in Germany, we recently started a collaboration with the Radiation Toxicology Laboratory at CEA in France. Upon completion of this project, we are pursing external funding to develop further the detector for a range of imaging applications that will span radiation biology, cancer treatment, and national security applications.

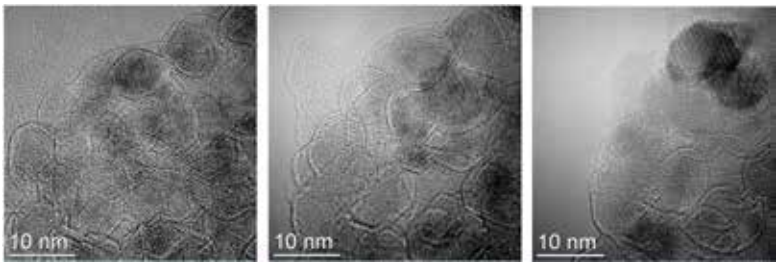
PN12012/2413

Correlation of Colloidal Interactions and Macroscopic Rheology in Concentrated Electrolyte Solutions

Jaehun Chun

Our goal is to develop a tool based on a fundamental understanding of particle interactions that allows either prediction of waste and blended waste rheology or manipulation and control strategies to render waste slurries to be less prone to solid stratification and accumulation.

Hanford tank wastes are radiological mixtures of insoluble and soluble solids in highly concentrated salt solutions. Colloidal interactions in these wastes can give rise to complex non-Newtonian waste rheology that must be considered during design and optimization of Hanford waste disposition processes. The rheology of colloidal dispersion in strong multicomponent electrolytes is expected to be governed by long-range ordering of individual particles or particle aggregates. Particle interactions in the most colloidal systems (i.e., single component mono-disperse spherical or other simple particle shaped colloids) suspended in dilute single component electrolytes are modeled using the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory, in which particle interactions are typically governed by attractive van der Waals and repulsive electrostatic forces. However, the DLVO theory cannot be simply applied to Hanford waste slurry. Its high dissolved salt content induces the loss of electrostatic repulsion as a result of double layer collapse. Further, owing to various dispersed phase minerals, aggregation can result from an electrostatic "attraction" between phases with opposite surface charges, in turn allowing non-DLVO effects such as steric hindrance and solvent structuring to control particle interactions fundamentally.



TEM images of dry boehmite particles: t=0 (left), t=125 sec (middle), and t=220 sec (right) under electron beam focusing with 200 keV.

This project will quantify these unique particle interactions to understand how they arise in terms of the chemical physics at solid-liquid interface and to determine how these interactions influence long-range ordering of colloidal waste particles and bulk suspension rheology in tank-waste-relevant systems. To limit test system complexity, a single solid mineral phase boehmite is selected for our study because it exists prevalently in tank waste and is problematic with respect to waste rheological properties. Colloidal interactions between boehmite particles will be measured directly under tank-waste-relevant chemical conditions using colloid probe atomic force microscopy (CPM) and modeled using theories/simulations that implement the relevant water and dissolved ion structuring at the particle-liquid interface. These research efforts are expected to allow coupling of physicochemical phenomena at different length scales involved in bulk rheology of colloidal suspensions that can establish a unique platform for obtaining physical insights for colloidal suspensions applicable for many suspension-based processes. Our ultimate goal is to develop a fundamental understanding of the particle interactions that allows either prediction of waste and blended waste rheology or manipulation and control strategies to render waste slurries easier to mix, transfer, and be less prone to solids stratification and accumulation.

The aggregate structure and its evolution will be investigated by *in situ* scanning electron microscope (SEM), implementing System for Analysis at the Liquid Vacuum Interface (SALVI), and transmission electron microscope (TEM) to couple particle interactions with the aggregate microstructure. The SEM and TEM tools will be used extensively in non-radiological and radiological environments, respectively. In addition, the rheology of the model suspensions will be characterized using a standard bench-top rheometer and a micro-rheometer based on SALVI. As a complementary tool, colloidal-scale simulations will be performed to link particle forces, aggregate structures, and bulk rheology, which would provide cross-validation.

PN15091/2766

While we mainly performed preliminary studies in FY 2015 for various aspects of the project, we also made the following findings: 1) the importance of water structures to colloidal forces; 2) radiation effects on boehmite particles via TEM; 3) identification of reasonable paths for simulations; and 4) preparation of setup for *in situ* SEM. The importance of water structure is a crucial finding because our hypothesis is that water structure is a key for particle interactions at conditions relevant to Hanford wastes. The effect of radiation is the first observation for radiation effects on boehmite, which ensures the possibility to study radiation effects on boehmite particle suspension via electron beam focusing.

In FY 2016, we will complete the setup for *in situ* TEM and SALVI and perform studies on radiation effects and microstructures of aggregates, respectively. We will also calculate water structuring on boehmite and transform it into dispersion interactions and study hydration forces for total interactions. Additionally, we will build a simulation framework (especially for particle interactions and radiation effects) and conduct a preliminary study with "sphere" approximations.

Detection of Production at the Source

Ronald P. Omberg

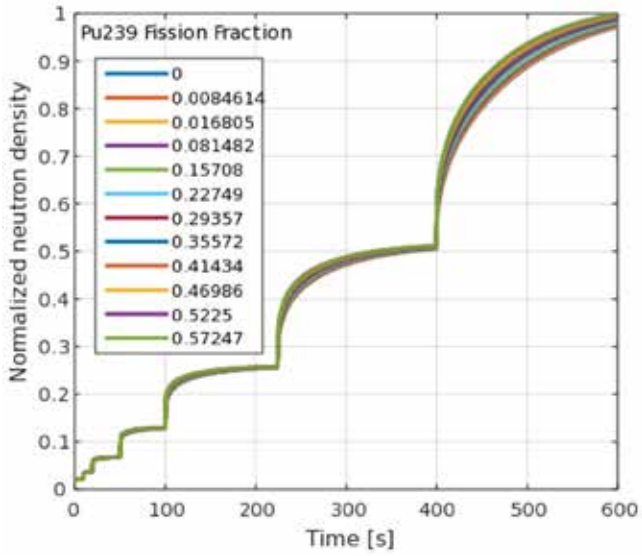
The objective of this project is to explore neutronic signatures that will unambiguously indicate if unauthorized use and production are underway.

Research reactors are often the first technology that a nation intent on producing unauthorized plutonium will procure. Larger research reactors can produce a significant quantity a year, if properly configured. This research will determine if such a reconfiguration will produce revealing transient operating signatures. Previous efforts to detect unauthorized use of a research reactor were based on a thermal or calorimetric balance on the primary heat transfer system. Such balances are technically known to be inaccurate and only determine the thermal power, the power at which the reactor is operating, rather than detecting unauthorized use. This project will examine the neutronic behavior of the reactor, which has the possibly of unambiguously detecting unauthorized production. The technical achievement associated with this project is to provide a signature technique that will allow declarations made by nation states to be validated with objective evidence such as reactor logs.

In FY 2015, we began by exploring the possibility that unauthorized use of a research reactor would produce a transient behavior with a revealing signature. It was found that such use would produce a different signature when the reactor is ascending to power after being shut down for refueling. The magnitude of the signature could very well be small, and accurate detection techniques may be needed if transient behavior is to be the only indication.

While performing this research, it was found that there may be possible other indicators of unauthorized use. For example, reactivity changes during an operating cycle and the associated control rod movements may be indicators. In addition, there may be neutronic detector locations that, when located properly, could provide additional signatures. The possibility that multiple signatures exist is important because multiple signatures will always provide more reliable objective evidence than evidence based on a single signature.

During FY 2016, this project will explore the possibility that these additional signatures could be either more revealing or can be used in concert with the transient signatures investigated in FY 2015. Each of these additional signatures will be investigated individually, and the combination of the entire set will be examined to determine the extent to which they will provide a conclusive determination of unauthorized use of the research reactor. Our goal will be to characterize these possibly new individual signatures and to develop a suite or combination of signatures that would clearly identify unauthorized use.



Signature effect of fissions in plutonium produced in a research reactor upon an ascent to power.

PN15019/2694

Development of a PNNL Underground Nuclear Explosion Simulation Tool

Justin D. Lowrey

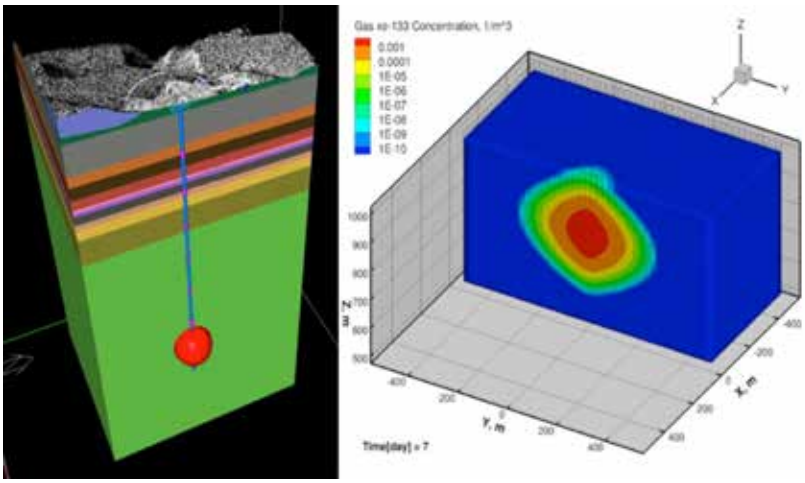
We seek to develop and demonstrate a PNNL simulation capability that will address some of the most challenging aspects of understanding post nuclear explosion environments and the evolution of underground nuclear signatures.

Monitoring the world for evidence of clandestine underground nuclear explosions represents a significant technological challenge and constitutes a major priority for the United States and international community. For over two decades, numerical underground gas transport models have been used to increase understanding of how post explosion gases migrate through the ground and leak at the surface. As the object of conducting nuclear activities underground is to contain them, the goal of developing such post explosion models is to explore how best to collect and target environmental samples that might indicate whether a nuclear explosion has occurred. This includes investigation of when, where, and how to look for explosion evidence and how to distinguish it from other civilian sources. A greater effort has been made in recent years to examine underground gas transport from a more fundamental level.

We are developing a simulation tool suite based on the PNNL Subsurface Transport Over Multiple Phases (STOMP) environmental fate and transport software capable of simulating post underground nuclear explosion scenarios by combining detailed nuclear, chemical, and environmental problem components. This tool will not only allow for realistic modeling of the physical geology, but also facilitate simulation of the complex geochemical and hydrological interactions that post nuclear explosion radionuclides can experience underground. The ultimate object of the simulation suite is to illuminate how these fundamental processes coupled with radioactive decay can impact large-scale mass transport following a nuclear explosion and potentially alter expected nuclear signatures.

Initial work in FY 2015 began with a broad assessment of current STOMP capabilities and deficiencies. Of critical importance to project success, this assessment included a detailed verification of STOMP's ability to handle radioactive decay chain processes through comparison with analytical solutions. This determination culminated in the successful running of a set of 3D test problems featuring coupled two-phase flow and transport of a chain decay series in aqueous and gas phases under non-isothermal conditions. An additional part of the assessment, equations of state used in STOMP were updated to cover a wider range of temperature and pressure conditions more suitable for its use in the underground nuclear explosion assessment tool. The revised equations of state provide more accurate estimates of the properties of water and steam under the extreme conditions immediately following a nuclear explosion.

A large-scale post explosion test case was developed consisting of a problem domain with variable geologic media, initial fission product deposition into the subsurface by high temperature and pressure, and using time-dependent Dirichlet gas and temperature boundary conditions determined by problem-specific weather input. This test case subsequently served as the model for defining the process flow for how to build generic scenarios and processing the large amount of output that results from such simulations. In FY 2015, development around this base case focused on input scripts and post-simulation analysis. Work in FY 2016 will attempt to integrate these various tools in a simple graphical user interface to enhance the user friendliness and focus problem scenario customization around those parameters and inputs most relevant to defining a post nuclear explosion scenario. This study will ultimately lead to an effort to implement uncertainty quantification within the underground nuclear explosion simulation tool.



Geologic environmental detail that can be used by the post nuclear explosion simulation tool suite being developed by this project. Left: an EarthVision geologic framework model incorporating detailed information about the problem domain; right: a 3D visualization of the ^{133}Xe gas concentration simulated from an explosive dispersal of ^{133}I in the ground with the concentration front breeching the surface.

PN15052/2727

D-T Neutron Generator Based Standard to Replace ^{252}Cf

James R. Hilliard

We are developing a neutron reference field for calibrating and testing personnel dosimetry and other neutron detection devices employed at nuclear power, DOE, and other neutron occupational environments.

Californium-252 is used nationally and internationally to produce neutron reference radiation fields for calibrating dose measurement devices because of its high specific activity. For emulating the occupational neutron radiation environments of various nuclear facilities, especially nuclear power plants (NPP), ^{252}Cf is placed within a sphere of heavy water (D_2O) moderator. The DOE loan/lease program for encapsulated ^{252}Cf sources ceased in 2012. Since then, replacement of high output sources for calibration has become cost prohibitive. Neutron generators (NG) based on the deuterium-tritium (D-T) fusion reaction provide high neutron fluence rates and may be feasible for use in replacing ^{252}Cf as a reference source for testing and calibrating neutron radiation measurement devices.

The focus of this project is to develop a moderating assembly capable of reshaping the 14 MeV neutrons from a D-T NG into a neutron spectrum resembling D2O-moderated ^{252}Cf or a more suitable NPP workplace spectrum. Additional neutron reference fields capable of simulating other neutron radiation workplaces may be possible through alterations in the shaping mechanism.

From a review of the D_2O-moderated ^{252}Cf neutron spectrum coupled with sample NPP spectra and radiation detector energy sensitivities, it was found that its neutron spectrum might not be appropriate for the calibration of all neutron detection devices, or unilaterally representative of all workplace spectra, even within the NPP environment. Simulations of several NPP dose measuring instruments calibrated using D_2O-moderated ^{252}Cf, indicated personnel dose estimates could range from 50% to 400%. Because of this large variation in potential response of detection devices calibrated using this spectrum, a revised NPP target spectrum – biased toward the energy regions responsible for the majority of dose equivalent – was developed as an initial goal for creating a moderated D-T NG spectrum.

In FY 2015, efforts were oriented toward a survey of moderating properties of several high- and low-Z materials, determining the neutron spectrum to be used as a target, identifying a scoring mechanism for grading candidate neutron spectra versus the target spectrum and, finally, the evaluation of a broad array of complex moderator designs. Based on a literature search, several moderating material candidates were determined, including high-Z materials (iron, copper, zirconium, tungsten, lead, bismuth, and depleted uranium) and low-Z materials (beryllium, polyethylene, carbon, water, heavy water, and Teflon®). Using Monte Carlo N-Particle (MCNP) simulations, evaluations were conducted of the neutron energy modification properties of these materials and optimal depths for retaining or enhancing neutron fluence and the production and energy of associated secondary gamma radiation.

Using the most promising of the materials evaluated, additional MCNP simulations of the transmission neutron spectra were executed based on a simple point neutron source model. These simulations considered combinations of between two and five layers (shells) of materials in a variety of thickness combinations. Material composites became more refined with experience in the simulation outcomes. At the culmination of this effort, 170 material combinations had been assessed, with the objective of matching the energy and shape of the broad peak of the NPP target spectrum while simultaneously minimizing the original 14 MeV peak. In addition, to aid in the objective assessment of the simulated spectra, a figure of merit was defined as the ratio of the root mean square score calculated based on the energy range from 0.4 eV to 10 MeV and the fraction of the total fluence in the considered energy range. Using this scoring mechanism, the top 10 moderator candidates were selected for further assessment of net properties.

An eventual working model of the selected moderator must account for the physical configuration of the D-T head and therefore will not be the same as the simple point neutron source simulations. Nevertheless, the results of this year's effort have provided the basis for constructing a working model for FY 2016, which will focus on methods to actively monitor the neutron output of the D-T neutron generator, a necessity for high-precision calibration applications.

PN15044/2719

Feasibility of a Dual-Wavelength, Dual-Scintillation Material Fast Neutron Detector Concept Using Bragg-Peak Peak Detection Physics

Jennifer E. Tanner

We are developing a detector that distinguishes between radiation events to enhance the capabilities of international nuclear inspection teams.

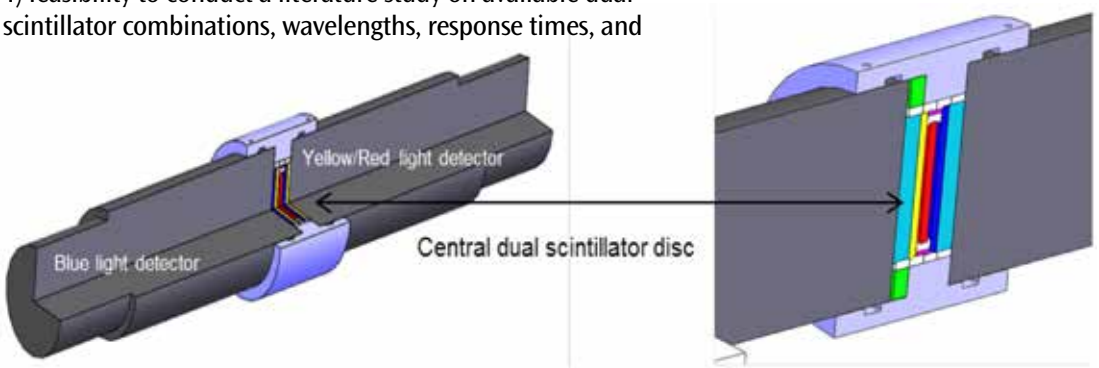
Detecting fast-neutron fields, especially imaging components in close proximity to such fields, is a key area for future development in support of treaty verification, safeguards, and national security. One of the challenges associated with detecting fast neutrons is distinguishing between fast neutron from gamma radiation events. The typical strategy for detection is to moderate the fast neutrons with thick hydrogenous substances like water or plastic to slow (thermalize) so they can be detected much more easily using common thermal-neutron detectors. This approach, however, results in the loss of energy, timing, and direction information of those neutrons and compromises their value as a signature.

In this project, we propose to develop a dual-scintillator radiation detector that is able to achieve this goal. Beyond simply spectroscopy, we envision that the technology could be used to develop imaging arrays, as fast-neutron spectroscopy and imaging technology could significantly enhance international nuclear inspection team capabilities. The present study is novel in that it leverages other variances between two different scintillators in a single composite. The method used is superior to other approaches because it allows one to discriminate against gamma events without discarding low energy neutron events. Our project consists of four phases: 1) feasibility to conduct a literature study on available dual-scintillator combinations, wavelengths, response times, and matrices; 2) modeling to calculate the performance of potential candidate material combinations; 3) fabrication to make the special dual-wavelength scintillator; and 4) prototype to build and evaluate performance.

Initially, the scintillating material selected for detecting both gamma rays and fast neutrons (e.g., via recoil protons) was an inorganic material with a peak scintillation wavelength response. The detecting gamma rays had an organic material that combined to produce a composite disc. The other main components of the test device were blue- and yellow/red-sensitive photomultiplier tubes (PMTs) and associated blue bandpass and yellow longpass filters to ensure each PMT was seeing only its respective light emission. The pulses from the PMTs were fed to a fast oscilloscope that could store large data sets and transfer them to a computer with spreadsheet software. Low activity neutron and gamma-ray sources completed the benchtop setup. A graphical representation of the detector is shown in the image.

Preliminary data collected from the benchtop test device revealed that in the presence of the gamma and neutron sources, blue-sensitive PMT provided a factor of ~100× net increase in pulse rate. Two different yellow/red-sensitive PMTs were tried, both providing zero pulses regardless of whether the neutron field was present. Preliminary testing suggests these PMTs are not functioning; therefore, a working yellow/red-sensitive PMT needs to be acquired to resume testing.

Additional testing is needed to show significant differences in ratios of pulse distributions from the dual scintillator, dual wave-length detector, and provide a high fast-neutron detection efficiency. Once achieved, a working prototype portable field device could be developed for the important uses described above, including nuclear warhead detection and imaging. Such a Bragg-peak neutron imaging detector is conceptualized as being made up of 1–2 cm diameter pixels in a 30 × 30 cm array, which could potentially provide up to four images, each representing one of the four energy ranges that make up the full energy spectrum (thermal, epithermal, intermediate, and high).



Benchtop test apparatus using the dual scintillator disc sandwiched in a light-tight chamber between blue- and yellow/red-sensitive PMTs covered with appropriate bandpass and longpass light filters.

PN15079/2754

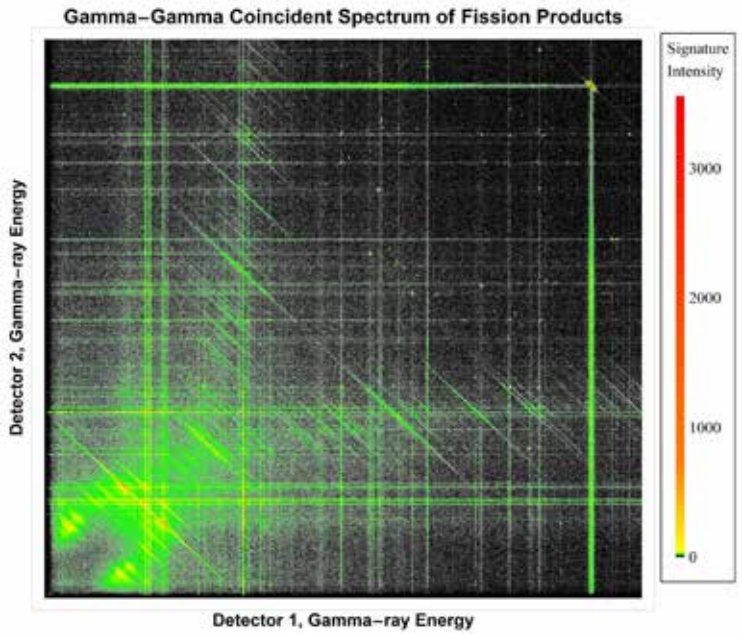
Gamma-gamma Coincidence Analysis Algorithms

Glen A. Warren

This project will advance our capabilities in gamma-ray signature analysis, enabling more efficient and accessible evaluation, in turn providing greater sensitivity than traditional single gamma-ray spectroscopy.

Gamma-gamma coincident signatures improve detection sensitivity of select radioactive isotopes in a variety of applications. It is particularly powerful for conditions that render single gamma-ray spectroscopy methods less effective: high backgrounds, high count rates, and low-resolution detectors. Coincident gamma-ray signatures have the potential to be exploited for a variety of nuclear science applications, including low-background measurements, post-detonation forensics, and environmental monitoring. Despite these proven advantages, the nuclear science community has been slow to utilize gamma-gamma coincident signatures in applied nuclear research. The main barrier to a large-scale use of this technique is the complexity of the analysis: no publically available tools are able to streamline the analysis, and there are few publications on the underlying methodology. Our project aims to reduce that barrier greatly by developing well-vetted algorithms for gamma-gamma coincident signature analysis. We will develop algorithms for this type of analysis, test them on simulated and real data, and publish our results.

There were three main accomplishments for the project in FY 2015. First, we completed a review of prior work in the field, including publications, existing analysis tools at PNNL, and engaging subject matter experts. This review confirmed that there is no existing solution to this problem, and that there is significant interest in the community in developing a solution. In addition, we commissioned two gamma-gamma coincident detection systems that increase PNNL's capability to perform gamma-gamma coincident measurements. These two systems enabled us in the project to test algorithms against well-known calibration sources and leverage a variety of experimental sources from other ongoing PNNL work. Finally, the project began work on algorithm development, identifying several possible algorithms. The ground work for a testing framework to evaluate algorithms has been developed. Simulated and measured data on fission products have been used to support initial algorithm development.



This spectrum shows the high complexity of data from a gamma-gamma coincident measurement of fission products. Color indicates signature intensity. The hundreds of round dots are signatures of interest, which need to be extracted from the complex underlying background.

For FY 2016, we will focus on developing and testing analysis algorithms. Several algorithms have been identified for further examination. To help vet algorithms, we will conduct measurements on the detector systems that were commissioned in FY 2015. We will aim to publish our findings on vetted algorithms in a peer-reviewed journal.

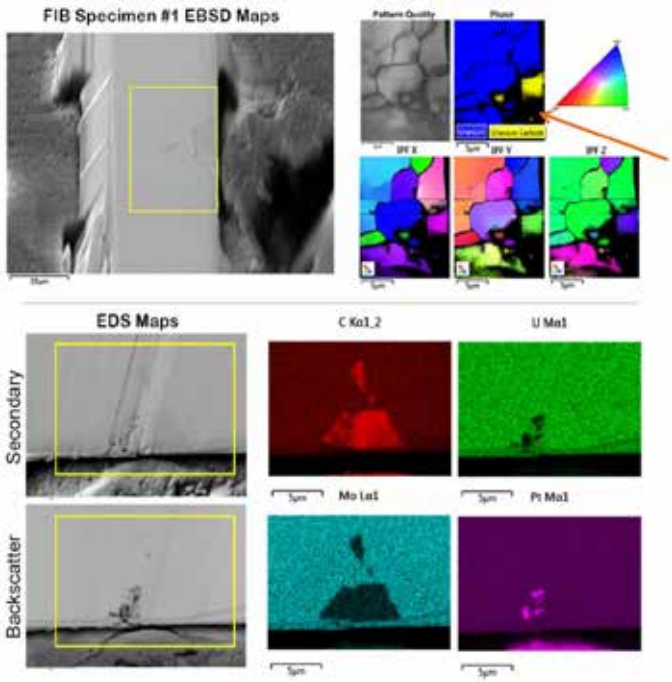
PN15071/2746

Hot Particle Analysis Aided by a State of the Art Focused Ion Beam

Dallas D. Reilly

This project seeks to use focused ion beam technology to subsample highly radioactive materials for analysis, advancing the capabilities for radioactive materials study around PNNL and the DOE complex.

The main intent of this project is to use a combination focused ion beam (FIB)/scanning electron microscope (SEM) to analyze and subsample highly radioactive materials for movement into laboratories and instruments at PNNL that do not currently or regularly accept highly radioactive samples. The Radiochemical Processing Laboratory (RPL) is a facility at PNNL that has the capability to perform chemistry and analysis on many radioactive materials up to very large quantities. However, it lacks in analytical capabilities in which other parts of the laboratory excel. Recently, a state-of-the-art FIB/SEM has been acquired for subsampling and analysis of radioactive materials. These instruments have been used previously in the semiconductor industry for microscopy sample preparation and analysis, but as radioactive material subsampling tools, they show much promise.



Example data from the low enriched uranium samples. Top right: EBSD maps that indicate grain orientations and structural phase of the two components, uranium metal and uranium carbide. Below: EDS maps of the same areas showing the relative concentrations of carbon, uranium, molybdenum, and platinum.

In FY 2015, our efforts are focused on various subsets of samples, including low enriched uranium metal fuels, used nuclear fuel remnants, and plutonium hot particles to prove the worth of this technology for national security, basic actinide sciences, and areas relating to the nuclear fuel cycle. The instrument installation has been only recently completed; because of that delay, low enriched uranium metal fuels, one of the target materials, was pursued at another facility that contains a FIB/SEM capable of working with uranium but not the other materials targeted for this work. Specifically, our primary objective for the low enriched uranium metal samples was spatial isotopic analysis via secondary ion mass spectrometry (SIMS) to investigate isotopic variations within the material. Samples were prepped for SIMS analysis and subsequently analyzed with another SEM for elemental composition via energy dispersive spectroscopy (EDS) and grain phase orientation via electron backscatter diffraction (EBSD). FIB/SEM preparation for SIMS analysis is not a traditional method, so establishing a protocol for this preparation was a new accomplishment. Obtaining EBSD data on these samples was also new, as there had been several previous unsuccessful attempts to obtain the samples. In total, three samples have been prepared for SIMS. As soon as the instrument is ready, samples will be moved to that facility and analyzed there.

In FY 2016, this work will continue at PNNL, with targets to subsample remnants from used fuel dissolution and plutonium hot particles. These samples will be moved to facilities to perform local electron atom probe and aberration corrected transmission electron microscopy. If successful, it will represent the first time there has been demonstrated analysis of these types of materials on those instruments.

PN15049/2724

MANDRAKE

Alex J. Stephan

We applied signature discovery tools to identify complex, non-traditional signatures for treaty verification to enhance current but outdated approaches.

International treaty verification currently relies on limited but long-standing methodologies utilized by analysts. These methodologies are static, labor intensive, and rely on the analysts' subjective opinion about the meaning of the observables. For this project, we demonstrated that the application of PNNL-developed signature discovery tools would aid treaty verification data analysts in the identification of complex, non-traditional signatures. The resultant novel signatures helped to discriminate between legitimate activities and potential violations of international treaties to enhance the current approaches used by the U.S. government. We developed competing hypotheses that were then built into signature discovery tools that provide the government with additional toolsets that will be both predictive and discriminatory.

We gathered data from multiple test cases of suspicious activity, extracted the observable data, and built a table of competing hypotheses against the defined outcomes. The competing hypotheses were then built into a Bayesnet of the observables. We then tested each dataset of suspicious activity against the Bayesnet to generate unweighted uncertainty assessments. When complete, the observables were weighted against the relative value of different observations for making assessment of the hypotheses. While each observable is of value, not all are of equal value. To illustrate, for a given test case, the presence of a truck may be observed at each potential treaty violation. However, a key observable may be a particular identifiable truck that is present only during treaty violations.

Once we were satisfied that the Bayesnet correctly characterized known datasets, we then subjected the Bayesnet to an uncharacterized dataset. The resultant output was analyzed to understand the likelihood part of the risk equation. The output could now provide a complex signature of the individual observables that is defensible, based on data metrics, and not subjective in nature. Next, we subjected the output of the model to signature discovery toolsets that generated the "likelihood" of a treaty violation. We believe that this activity would generate predictive temporal data that will be of great value to the analysts.

We were able to demonstrate successfully that we could:

- develop observables of known events
- use signature discovery tools to characterize the observables
- develop complex, non-traditional signatures from observable data
- weigh the observables to provide the likelihood of a treaty violation, and
- develop a time-series of the data for the temporal probability of an event.

PN15060/2735

Modeling the Long-term Degradation of Spent Nuclear Fuel Dry Cask Canisters

Ram Devanathan

This project has advanced multiphysics modeling for the safe, long-term storage of spent nuclear fuel (SNF). The benefit of this research is a more reliable prediction of the time period in which SNF can remain in dry storage at various locations around the country.

It is becoming increasingly evident that SNF will be maintained in extended dry storage within a steel canister surrounded by a concrete cask for 100 years or longer. Following this "interim" storage at a nuclear power plant site, SNF will be transported to a permanent geological repository if one becomes available. During dry storage, material degradation can initiate on the outside of steel canisters from external and internal surface temperatures, residual stress (especially near welds), environmental conditions (e.g., humidity, concentration of atmospheric contaminants), and canister material composition and surface finish. At present, we lack the mechanistic understanding needed to provide assurance that SNF canisters will not degrade during storage and maintain integrity during transportation. We also lack the scientific basis to predict the time period within which SNF can be safely held in dry storage at different locations.

The objectives of this project are to identify the atmospheric contaminants that play a key role in stress corrosion cracking (SCC) of steel at various locations in the United States and evaluate the mechanisms for contaminant deposition on the canister surface by collecting available data and refining existing models. This work can be integrated to develop a predictive model of canister degradation with an evaluation of canister surface temperature profiles, mean atmospheric temperatures, humidity levels, and stresses that a model canister will experience. The broader impact of this work is that it will improve our understanding of the environmental conditions that affect material degradation and increase confidence in the performance of SNF dry storage and transportation systems.

In FY 2015, we used DUSTRAN, a PNNL-developed dust dispersion modeling system, to model the deposition of chloride, the primary contaminant of interest for SCC, from sea salt aerosols on a steel canister. Results from DUSTRAN simulations run with historical meteorological data were compared against measured chloride data at a coastal site in Maine. This work calculated particulate emission rates for area sources using an open-ocean source function from the literature. Emission rates were generated using three sets of wind speed data as inputs for this function obtained from two offshore buoys maintained by the National Oceanic and Atmospheric Administration local portal. In addition, efforts commenced to improve the modeling of SCC initiation and growth in stainless steel canisters.

The modeled concentrations were greater than but within an order of magnitude of those measured at the Maine site. It is believed that the simulations may have been biased toward higher emission rates because of the use of offshore wind speeds. It has been observed that these wind speeds decrease as distance to shore decreases; thus, the emission rates were perhaps an overestimate of the entire area source. Time-series analysis revealed a cyclic pattern in wind speeds consistent with meteorological observation, and a similar cyclic pattern was observed in concentration. The conclusion is that the use of a single emission rate across the entire simulation duration of 1 week is not reasonable. A statistical analysis of average emission rates calculated for both buoys revealed standard deviation greater than the mean in all cases, further suggesting that the set of single emission rates did not accurately represent the time periods simulated.

The surf-zone, defined as the location of wave breaks, will have a greater contribution to the production of sea salt aerosols than open ocean. Future modeling will account for the differences between surf-zone and open-ocean sources to avoid overestimating emission rates. In the current work, the averaging of wind speeds decreased discrepancies between measured and simulated concentrations by eliminating high wind speeds from the open-ocean and factored in wind speeds more representative of the surf-zone.

This work has resulted in three conference presentations, and a journal article is being prepared. Comparisons of simulated and measured data have shown the potential of DUSTRAN in predicting the dispersion of atmospheric chloride from sea salt aerosols. Though modeled concentrations were greater than measured concentrations, the decrease in error as the level of data abstraction decreased suggests that both further refinement in the software system and more detailed input would result in more accurate predictions. Work is underway to connect the model discussed above with a materials degradation model to develop an integrated modeling scheme for SCC.

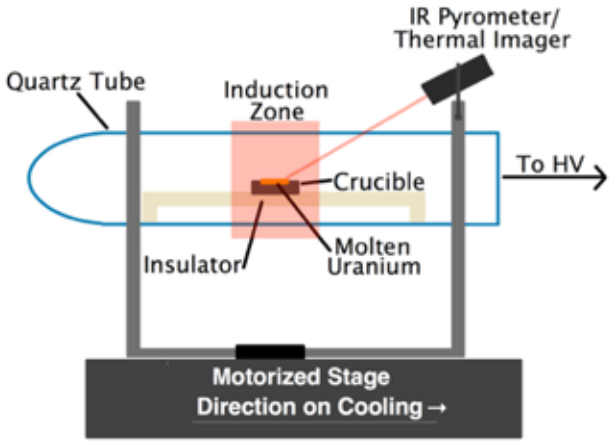
PN15033/2708

Monitoring Diffusion of Actinide Daughters and Granddaughters in Metals for Chronometer Applications

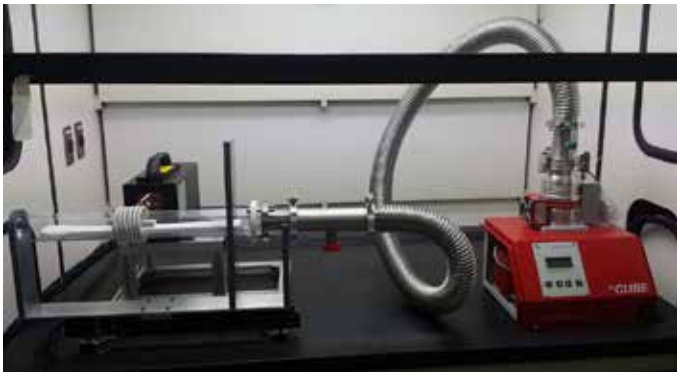
Dallas D. Reilly

This project seeks to understand trace fractionation with a focus on radiochronometer daughters to inform investigators about illicit nuclear material. Understanding and application will bolster forensics programs and broaden our scientific knowledge of nuclear materials.

This work seeks to develop a mechanistic understanding of the chemical and physical processes controlling parent/daughter fractionation during the casting of uranium (U) and other metals by performing controlled experiments and modeling to provide a theoretical basis for these fractionations. Initial experiments will involve the induction melting of U metal samples, followed by slow extraction from the induction zone to produce a temperature gradient during cooling. This controlled gradient will allow migration of thorium (Th) and other trace elements. Secondary ion mass spectrometry (SIMS) will be used to probe Th concentration on focused ion beam "lift-outs" from the metal.



General schematic of the induction system.



Current state of the induction furnace system. The RF induction furnace can be seen on the left, along with the motorized drive stage and quartz cell containing the alumina insulator and inert matrix-coated graphite crucible. The high vacuum system is on the right.

The aforementioned sampling will allow for analysis both as a function of depth (~20 μm into the surface) as well as along the temperature gradient. Concentration gradients of Th and trace elements discovered via SIMS will enable a competent modeling effort, which will be applied to other parent/daughter series in the future. The results of this work will provide the framework for developing a predictive capability and the scientific basis for interpreting chronometer measurements on actinide materials with unknown processing history.

This project started in mid-year FY 2015, during which time an induction furnace was constructed. The experimental setup includes a 3.5 kW radiofrequency induction furnace, a cooling system, quartz cell with inert matrix-coated graphite crucibles, alumina insulators, high vacuum system, argon purge system, motorized drive stage, and thermal imaging system. In addition, we have written procedures that are currently being reviewed for experiments for both non-radioactive surrogates and uranium metals. Overall, the project is on track to meet or exceed the deliverables set out in the initial proposal, including testing the system with non-radioactive surrogates and setting up the computational framework for modeling efforts.

PN15095/2770

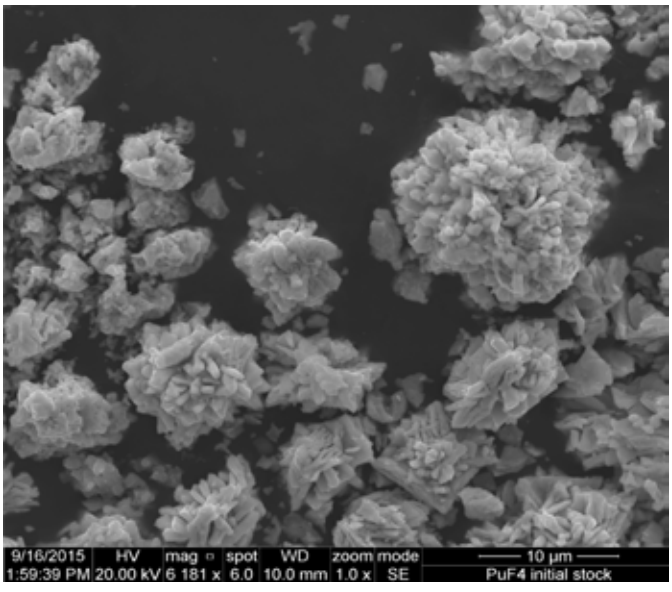
Signatures of PuF_4 and Pu Metal Processing

W. Karl Pitts

The goal of this project is to reconstitute subsets of Hanford's Plutonium Finishing Plant (PFP) processes used to produce plutonium (Pu) metal and recover Pu from various waste forms.

The production of plutonium metal from plutonium fluoride (PuF_4), its shaping and forming, and the recycling of scrap materials are all of interest to the nonproliferation community. These production steps are beyond those required to form plutonium oxide for mixed-oxide (MO_x) reactor fuel and are indicative of weaponization activities. However, these same processes might be used legitimately to produce metallic nuclear fuel for fast reactors. Specifically, PNNL is converting most of the last remaining PuF_4 to Pu metal in order to understand the process that was used to produce Pu metal and weapons components at Hanford's PFP during the Cold War.

During FY 2015, legacy material was analyzed using a variety of analytical techniques, including gamma energy analysis, alpha energy analysis, thermal ionization mass spectrometry, diffuse reflectance (DR) spectroscopy, optical microscopy (OM), scanning electron microscopy/energy dispersive X-ray spectroscopy, thermogravimetric differential thermal analysis (TG/DTA), and X-ray diffraction (XRD). These analyses confirm that the material was chemically separated from other radioactive materials in late 1966 with subsequent conversion to PuF4. Numerous characterizations (DR spectroscopy, OM, TG/DTA, and XRD) show that while the PuF_4 has undergone metamictization during its 50 years of storage as a reference neutron source, it has retained its particulate morphology and structure known from historic studies performed at the PFP.



PuF_4 morphology comprised of mostly spherical "rosette" structures with high surface area.

The material will be reduced to metal by reacting it with calcium metal at high temperatures in a reaction similar to a thermite process. Calcium metal, iodine, and PuF_4 are placed in a crucible and heated in an induction furnace. The conversion starts with reaction of calcium and iodine whose supplemental heat initiates the reaction of calcium with PuF_4 to form plutonium metal, which separates from the slag and forms a button at the bottom of the crucible. This process was developed at Los Alamos in 1944 during the Manhattan Project. The PNNL system uses a custom designed induction furnace that is compatible for installation into a glovebox certified for plutonium operations. In addition to the induction coil, the system includes a vacuum and inerting chamber to maintain atmosphere inside and around the reaction vessel, a load cell designed for sealing the reaction vessel and serving as pressure relief, and temperature control using an infrared pyrometer with a thermocouple readout for over-temperature control. The apparatus will be installed in the glovebox during FY 2016.

The preparation process includes cold tests with a cerium fluoride surrogate during the last quarter of FY 2015. The first test was a complete checkout of the containment and venting system with a CeF_4 reduction. Additionally, this test showed that the system operated as expected and a mix of cerium metal and slag was produced. While a high purity metal was formed, it did not coalesce into a button at the base of the crucible. This activity was expected, as the initial test did not use optimized materials. The next tests will use finer calcium and larger charges that will lead to better separation. The irreplaceable PuF_4 will not be reduced until cerium buttons are reproducibly produced with the CeF_4 reduction process. The first plutonium reductions are expected toward the beginning of the 2016 calendar year.

PN15037/2712

Signatures of Underground Explosions (SUE)

Timothy A. White

We are in search of non-traditional signatures that indicate a chemical explosion rather than rely on the absence of nuclear debris to indicate that an event was chemical in nature.

Should the International Monitoring System detect an apparent underground explosion that lacks the necessary radionuclide signatures necessary to confirm a nuclear event, the question will be which signatures should be exploited to determine whether the event was a chemical rather than nuclear explosion. Discovery of signatures and development of tools that can be used to discriminate underground chemical from nuclear explosions will provide government agencies with the tools to enhance national and international security. Investigations and experiments into these potential signatures will also leverage the science and discovery base at PNNL and enhance our capabilities and expertise.

Identification of signatures used to discriminate underground nuclear from chemical explosions will be a demonstration of the signature discovery process that is

- more efficient by carefully defining the proposition, specifying the scenarios, and developing a process to use limited resources of subject matter experts (SMEs) efficiently
- more economical by documenting a method for exploring the discovery process that will be applicable to other problems, and
- more rigorous as we work potential signatures down through the process to demonstrate developed tools for measuring signature quality and experimental design.

The process for investigating signatures of underground explosions began with brainstorming by a breadth of SMEs and a parallel investigation at the Defense Threat Reduction Information Analysis Center for prior work (primarily nuclear testing) that could be used to guide or impact our investigation. The brainstorming results were followed by a distillation of key ideas to a list of eight categories of observables as shown in the table that are phenomena that could rise to the level of signature but require investigation to explore the order-of-magnitude effects and potential for discrimination. The categories were addressed in targeted white papers by "signature champions." These documents were used to choose small projects for the characterization of specific potential signatures.

Investigations were initialized in the chemical degradation products and patterns of life categories. The chemical degradation work is focused on cataloging the gases released from detonation of ammonium nitrate and fuel oil, concentrating on less ubiquitous chemicals. The patterns of life group examines a variety of observational data in the pre- and post-detonation time frames that may differ between the types of events.

Early in FY 2015, it was determined to end this project and initiate two independent follow-on projects. One of those focuses on an in-depth investigation into molecular fingerprints of chemical explosions, while the other is related to patterns of life. Those are reported elsewhere in this document.

Category	Chemical Explosion Observable	Nuclear Explosion Observable
Chemical degradation products	Hundreds of tons of CO_x, NO_x, and unique products	Very little
Thermal	Thousands of degrees	Hotter than the sun
Post-test ground effects	Extended source, "pushing" force	Point source, sharp force
Stable-isotope ratios	Introduce C, N, O from external source	Produce ^{14}C, ^{3}H
Electromagnetic pulse/ radio frequency	Small signal, larger if decoupled	Large signal
Patterns of life	Infrastructure for kilotons of chemical explosive	VIP activity
Biological	Poisonous CO_2 levels	Uptake of ^{3}H
Classic test signatures	Seismic, infrasound, hydroacoustic	*Radiological*, seismic, infrasound, hydroacoustic

Categories of observables to determine either chemical or nuclear explosions

PN14031/2615

Solving the Pu-238 Problem

Jeffrey A. Katalenich

We are working to improve fabrication techniques for radioisotope heat sources to enable future space exploration missions that rely on plutonium for heat and power.

Current techniques for producing plutonium-238 (Pu-238) oxide heat source pellets are based on powder processing that generates dispersible plutonium powders. Processing Pu-238 oxide powders in gloveboxes and hot cells results in plutonium dust dispersal and increased potential for a breach in the engineered containment. To solve this problem, PNNL is investigating sol-gel techniques as a way to keep plutonium in solution until macroscopic oxide microspheres are formed, eliminating the powder generation and handling steps. Our research is focused on demonstrating the production of Pu-238 microspheres and the feasibility of pressing these spheres into heat source pellets. Production of Pu-238 oxide microspheres by internal gelation has not been previously attempted, so project tasks include determining the optimal chemical parameters, desirable gelation conditions, and modifications to equipment for glove box operation.

To demonstrate the production of Pu-238 sol-gel microspheres and subsequent pellet pressing, work is divided into three main tasks in parallel. First, we are bringing a new glove box in the Radiochemical Processing Laboratory (RPL) operational to process gram-quantities of plutonium. Second, we are developing the optimal process chemistry for neptunium and plutonium using gram-quantities in a glove box. Third, we are establishing a non-radioactive sol-gel apparatus in the Applied Process Engineering Laboratory (APEL) as a testbed for new sol-gel equipment and procedures.

Sol-gel chemistry and solution preparation methods are established for cerium and uranium, but a technique for producing plutonium-only feed solutions has not been published. To develop a method for preparing plutonium oxide microspheres, we began developing procedures using a neptunium-237 (Np-237) surrogate material. This work has led to a procedure for preparing a feed solution with the relatively low acidity and high metal ion concentration that is required for effective internal gelation to occur. With the initial stages of chemistry optimization complete for neptunium, we are beginning work with plutonium-239 (Pu-239), which will proceed in parallel with continued Np-237 experiments.

Neptunium nitrate being loaded onto an ion exchange column for purification.

To establish a non-radioactive sol-gel capability at PNNL, previous sol-gel equipment was disassembled, and the parts were used to build a new device for microsphere research using cerium oxide. We are using the non-radioactive sol-gel apparatus to test new hardware and processing techniques prior to implementation with radiological materials in the RPL.

In FY 2016, we plan to iterate the radiological sol-gel apparatus design based on test results in the APEL and install the new apparatus inside of the glove box containment. Once non-radioactive testing using cerium oxide is complete in the RPL, microsphere production will begin with radioactive materials. We also plan to complete gelation experiments to determine the optimal feed solution parameters for Np-237, Pu-239, and Pu-238. We will use cerium oxide spheres to determine desirable microsphere sizes and densities for producing pellets and use the results to decide upon initial processing parameters for future work pressing plutonium pellets. A near-term task includes testing non-flammable washing solutions to replace flammable and toxic materials used in the current microsphere washing process. By the end of FY 2016, our goal is to have produced microspheres of Np-237, Pu-239, and Pu-238 to support plutonium pellet pressing studies in FY 2017.

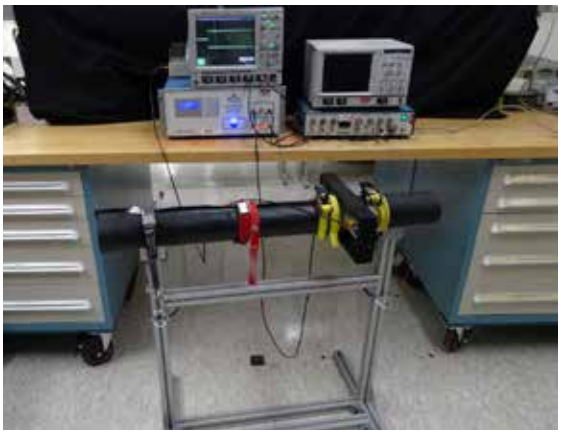
PN15027/2702

Technologies for Non-Intrusive, Unattended Measurement of UF_6 Gas Flow

Glen A. Warren

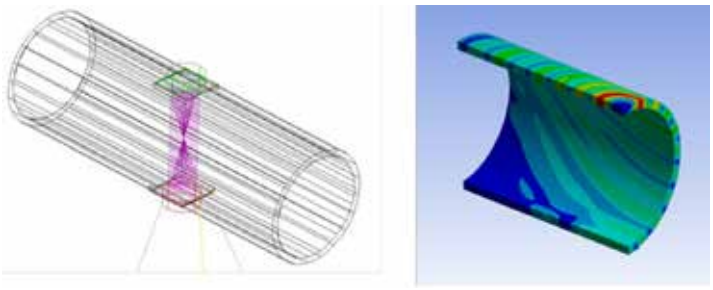
This project is a viability study of non-invasive techniques to measure gas density and mass flow rate in cooperative verification scenarios.

Expanding global uranium enrichment capacity under international safeguards presents challenges to the International Atomic Energy Agency (IAEA) and regional safeguard authorities (e.g., Euratom) to safeguard gaseous centrifuge enrichment plants effectively while working within budgetary constraints. A key enabling capability in the safeguards approaches being considered by the IAEA is high accuracy, non-invasive unattended measurement of uranium hexafluoride (UF_6) gas density and mass flow rate. At present, the IAEA has no unattended technology to meet this need.



Laboratory test station with pipe section, custom coupling fixtures and various noise-reduction provisions.

This project is a viability study on the use of acoustic technologies to noninvasively measure UF_6 gas density and mass flow rate in the header pipes of enrichment plants. The acoustic techniques rely on the interaction of applied acoustic energy with the flowing gas to enable assay of gas parameters (e.g., density). Transmit-receive methods have been used in other fields for measurement of flowing gas, but the enrichment-plant UF_6 scenario presents significant challenges for accurate acoustic assay. Primary among them is that the very low nominal gas pressure, approximately100 times lower than commercially available acoustic measurement systems typically operate, creates a large acoustic impedance mismatch between the metal pipe and the gas. This mismatch means that the transmission of acoustic power directly through the pipe walls, into the gas, and to the receiver is very low. This relatively weak interrogating signal must be discriminated from a relatively high background noise produced by the acoustic energy that propagates directly to the receiver through the walls of the pipe. The enrichment-plant scenario is further complicated by temporal variations in gas pressure and density as a part of normal plant operations.



Simulation of acoustic energy propagating directly through the gas (signal) and through the pipe (noise).

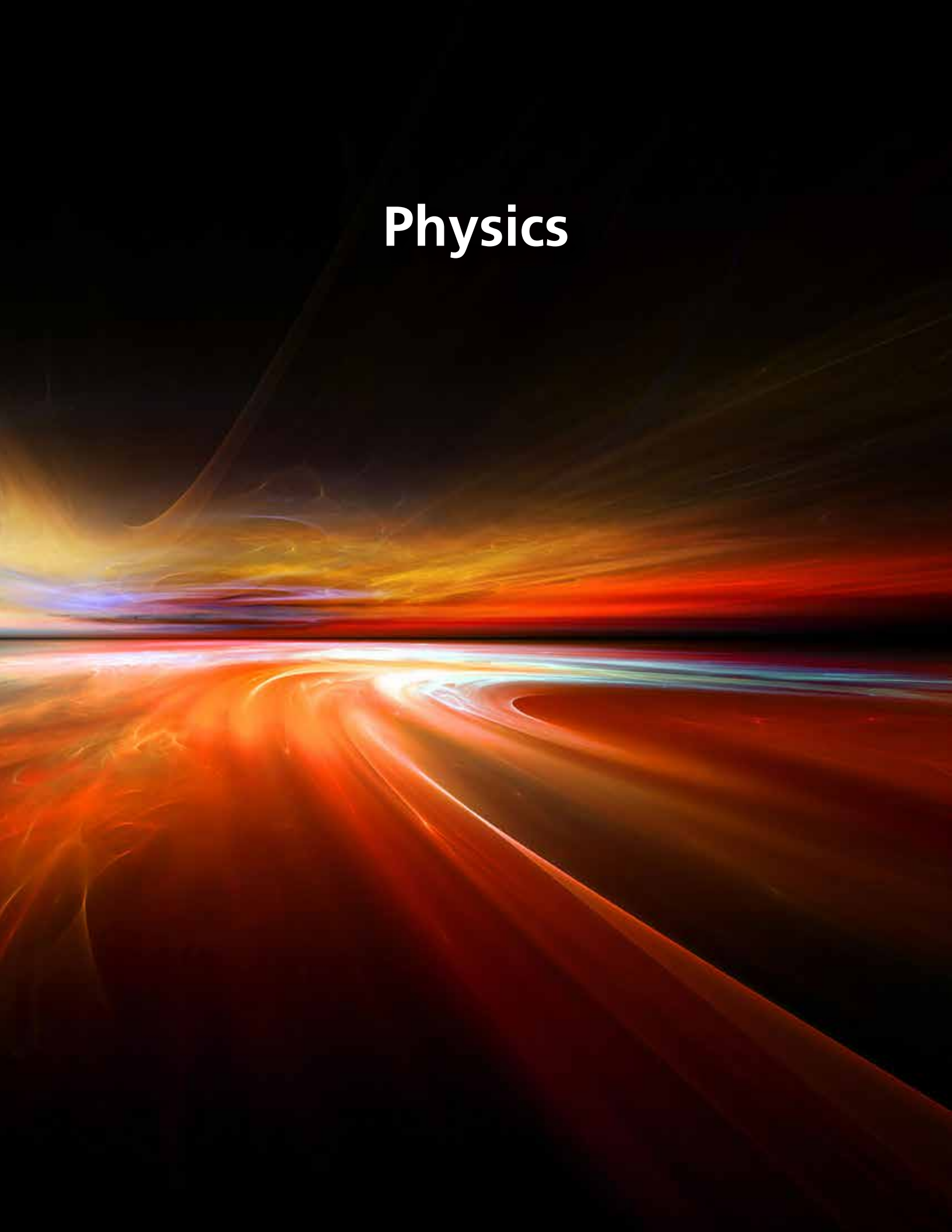
An extensive review of published research activities and commercially available acoustic flow measurement systems was performed to understand the state-of-the art focus the study and collect the UF_6 acoustic parameters needed to support simulation, measurements, and analysis.

A simulation framework was developed to explore methods systematically for increasing the signal and discriminating the background, such as careful placement of transducers to enhance signal collection while reducing noise collection, damping materials to reduce the noise component selectively, and encoding transmitter signals. Two-dimensional simulations support rapid, preliminary exploration of design options; more computationally intensive 3D modeling provides high fidelity insight into the strengths and weaknesses of realistic instrument designs. To complement the predictive modeling, a laboratory test bed was developed. A combination of commercially available transducers, custom mounting fixtures, and flexible noise-reduction provisions allow for the exploration of innovative system designs and benchmarking of the predictive modeling results.

There were three key findings for this project. First, it was determined that mitigating the signal that passes through the pipe wall is critical to a successful mass flow rate measurement. Second, it is likely that relative measurements with respect to a baseline will be necessary. Finally, measurements suggest that gas density quantification is viable.

PN14014/2598

Physics



Anthropogenic Uranium Detection with X-ray Microscopy

Andrew M. Duffin

To support nuclear materials analysis, we are developing new tools and techniques for analyzing uranium chemically on the nanometer spatial scale.

Each year, a considerable amount of research is conducted to detect and analyze anthropogenic uranium, often in a natural uranium background. Most of these studies ignore the chemical form of the sample and rely on mass spectroscopy to gain isotopic information. Unfortunately, this oversight leads to wasted efforts analyzing natural uranium minerals. Recently, researchers at synchrotron facilities have developed and employed sophisticated techniques for analyzing samples with X-rays. These experiments yield valuable information about electronic structure and chemical bonding.

The objective of this research is to determine the utility of X-ray microscopy for enhanced analysis of anthropogenic uranium. We are employing advanced X-ray tools developed at synchrotron light sources for identification of different anthropogenic and natural chemical forms of uranium. We will analyze relevant natural and industrial uranium compounds for fingerprinting purposes. Given the proper signatures, spatially resolved X-ray absorption spectroscopy could efficiently and non-destructively screen samples for anthropogenic uranium, allowing for subsequent isotopic determination. The results of our research will be of great interest to DOE and could fundamentally improve anthropogenic uranium analysis.

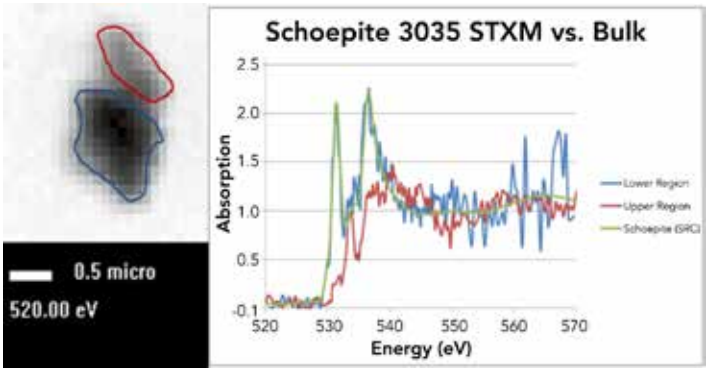
FY 2013 focused on obtaining preliminary X-ray absorption data on a test set of uranium minerals and developing methods for preparing the anthropogenic uranium samples. We restricted our time to collecting spectra at the oxygen K-edge, as this region promises the most chemical information. Indeed, the pre-edge peak position correlated with the chemical environment or uranyl species; i.e., oxygen K-edge spectra exhibit potential to differentiate various chemical forms of uranium.

Our FY 2014 goal was creating a library of reference spectra over bulk compounds to compare to future scanning transmission X-ray microscopy (STXM) measurements. We measured the oxygen K-edge absorption of a variety of uranyl minerals, including uranyl silicates, oxyhydroxides, carbonates, and phosphates. We also collected spectra for anthropogenic uranium compounds including uranyl fluoride, chloride, and nitrate. We found that the general classes of uranyl compounds (silicate, oxyhydroxide, carbonate, or phosphate) can be reliably distinguished on the basis of their X-ray absorption spectra. In all cases, X-ray spectra derived from uranyl minerals were distinct from the spectra obtained from uranyl fluoride and uranyl chloride. Comparison with the X-ray absorption spectra of appropriate model compounds (e.g., sodium bicarbonate for the uranyl carbonates) allowed the assignment of particular transitions to either the counter-ion or the uranyl moiety.

After establishing bulk spectroscopy and proving the ability of ligand near edge X-ray absorption fine structure (NEXAFS) to distinguish uranyl samples chemically, we worked to confirm the spectral integrity on the nanoscale. For this purpose, we collected STXM data at the Advanced Light Source over a schoepite particle sample. These results show excellent correspondence with the bulk schoepite spectra. In addition, the spatial resolution of the instrument can distinguish schoepite from a nearby contaminant.

In FY 2015, we continued STXM measurements on chemical reaction interfaces with analysis of uranyl fluoride particles deposited onto silicon nitride windows and artificially aged under 80% relative humidity for 2 months. For larger particles (~500 nm and up), the data showed changes from uranyl fluoride at the particle core to uranium oxide at the periphery. The smaller particles showed no spectral changes, indicating that these particles completely converted from the fluoride to the oxide. TEM-EELS data also provided the first evidence of an oxyhydroxide intermediate in this reaction chain.

These results show proof-of-concept for the ability of advanced chemical imaging techniques to chemically age-date reactive uranium particulates.



STXM data image at 30 nm resolution collected over two adjacent microparticles (left) with extracted spectra (right). The spectrum derived from the schoepite particle (blue) compares well with the schoepite spectrum from our reference library (green) and is distinguishable from a nearby contaminant (red). These results demonstrate how STXM can be used to classify individual particles in an inhomogeneous sample.

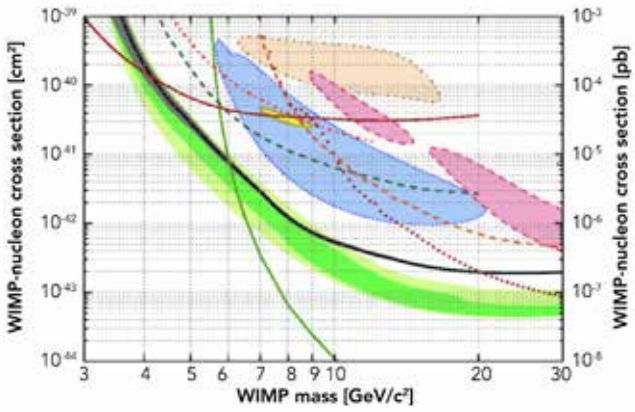
PN13027/2508

Dark Matter Physics

Jeter C. Hall IV

The dark matter that makes up 85% of matter in the universe is unknown. This project focuses on analysis of current data and future experiments to address this scientific priority in the field of cosmology and particle physics.

The nature of the matter in our universe is currently unknown. Cosmological observations on scales of galaxies to galaxy clusters to the thermal photon relic of the Big Bang suggest that the standard model of particle physics accounts for a mere 15% of the content matter of the universe. Baryonic matter has been largely ruled out as a candidate for dark matter, which leaves new stable fundamental particles as the favored possibility. Weakly interacting massive particles (WIMPs) are a broad class of fundamental particles similar to the neutrino that are proposed as a solution to the dark matter issue. Fundamentally, if there is a new symmetry of nature, then there could be massive, stable particles filling the universe with limited interactions with normal matter.



From a recent Physical Review Letters article, the above illustrates the scientific impact of recent SuperCDMS data. The black line shows the data sensitivity to the blue region of interest; the red shows low-mass WIMP sensitivity of the high-voltage operational mode proposed and led by scientists at PNNL.

Through this project, we established critical roles in the community effort to make progress in dark matter. PNNL is now a member of a number of large collaboration dedicated to searching for WIMP dark matter, MiniCLEAN, DarkSide, SuperCDMS, and PICO. SuperCDMS uses unique germanium detectors to search for dark matter interactions. SuperCDMS uses cryogenic bolometry to identify background events. PNNL scientists have recently published SuperCDMS data using a novel, high-voltage technique to search for light (<5 GeV) WIMPs. DarkSide and MiniCLEAN approach dark matter detection using 500 kg of liquid argon as the target material. The scintillation light of liquid argon fundamentally contains information on the nature of particle interaction. Although MiniCLEAN is a large dark matter detector, it is a small but critical demonstration for the envisioned third-generation experiment, a high priority long-term strategy of the high energy physics community.

PNNL's expertise in ultra-low-background materials helps to reduce the natural and cosmically induced background that could overwhelm the extremely rare dark matter events, which is the common challenge for all these experiments. PNNL's expertise in copper electroforming, uranium and thorium assay and detector assembly are helping these experiments make order of magnitude improvements in sensitivity.

In addition to the low energy signals, a dark matter signal is expected to vary annually due to the earth's orbit varying with respect to the Milky Way's center. PNNL developed a maximum likelihood analysis technique to search simultaneously for the low energy and time varying signature of dark matter interactions in deep underground experiments. The software analysis method development is a sufficiently generic enough analysis method that can be applied to future dark matter experiments.

In addition to participation in the planning, execution, and analysis of large, complex experiments to detect dark matter, PNNL is involved in detailed calculations to determine the ultimate sensitivity of specific approaches to WIMP detection. Scientists are using modern computation techniques to estimate the backgrounds produced in unavoidable high energy, cosmic ray interactions. Additionally, scientists are calculating the signals that are expected from the lowest energy interactions in semi-conductor detectors, a crucial detail that has no data and no theoretical predictions. With these two calculations, both the signal and the backgrounds will have better predictions, leading to a better understanding of the ultimate sensitivity of future experiments.

In FY 2015, we focused on generation one dark matter projects PICO and SuperCDMS and cross-cutting transformational technology. New analyses with these generation one dark matter projects were published or submitted to journals. The sensitivity to dark matter in the region illustrated in the figure has improved by an order of magnitude due to these studies. We additionally started a new investigation of distributed computing technology for small dark matter projects with good preliminary responses from the broader scientific community.

PN14006/2590

Discovering CENNS in MiniCLEAN at Fermilab

Andrew Hime

The detection and study of the coherent elastic neutrino nucleus scattering (CENNS) will open a broad window to previously unexplored regimes in neutrino physics.

CENNS is a fundamental process in the standard model of elementary particle physics, yet it has eluded detection since it was first predicted over four decades ago. Innovations in dark matter detector technology in concert with the Booster Neutrino Beam (BNB) at Fermilab now make the unseen CENNS testable. Key to measuring the CENNS is a detector with a sufficiently low-energy threshold to reveal a clean nuclear recoil signal that is free of background. The basic approach we have taken for the direct detection of dark matter has culminated in the design and construction of the MiniCLEAN detector. The detector requirements for a CENNS measurement are strikingly similar to that for dark matter detection, however, with a key difference: dark matter detectors need to be operated deep underground and free of cosmic ray-induced background while a CENNS detector would be placed near the surface in a neutrino beam with its associated beam-related backgrounds.

The technical approach and methodology focus on the primary detector performance parameters for a single-phase liquid argon detector as it concerns the challenges for measuring CENNS in a neutrino beam at Fermilab's BNB. The technical outcomes are congruent with the need to establish a detector with sufficiently low energy threshold to afford meaningful sensitivity of the CENNS signal. The ability to reach this energy threshold hinges on a complete understanding of the light yield and radioactive backgrounds at the analysis threshold, and the related experimental uncertainties that translate to uncertainties in the measured cross-section and differential energy spectrum. The results from the research supported by this project will define the capabilities for mini cryogenic low energy astrophysics with noble (MiniCLEAN) and future detectors scaled in target mass using the CLEAN liquids technology.

In FY 2015, we evaluated nuclear-recoil scintillation efficiency in light of available data and revised the model accordingly. We calculated Coulomb corrections to 39Ar beta spectrum, modeled uncertainties, and evaluated uncertainty in energy scale impact on precision in CENNS cross-section and differential energy spectrum measurements. Additionally, we defined requirements for water shielding and active muon veto and evaluated the costs and project plan for moving MiniCLEAN from SNOLAB to Fermilab.

Installation of the MiniCLEAN detector deep underground at SNOLab. Presently under commissioning, this prototype detector of dark matter by design exhibits all of the salient specifications for a CENNS detector. Performance of MiniCLEAN in concert with simulations will provide the necessary testbed of data to evaluate capabilities for future CENNS experiments.

Future work includes benchmarking the light yield model and the radioactive background model against data from MiniCLEAN. Additionally, we will construct a project plan for the first generation CENNS experiment.

PN15030/2705

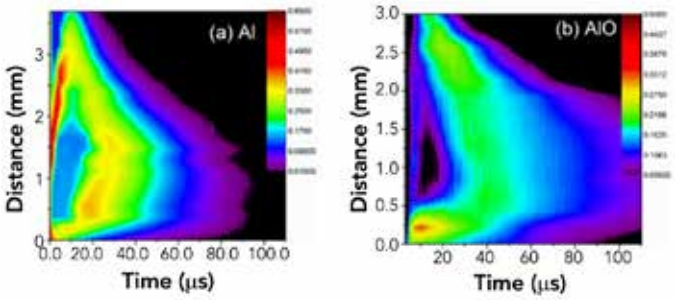
Laser-ablation Based Multimodal Tool for Nuclear Forensics

Sivanandan S. Harilal

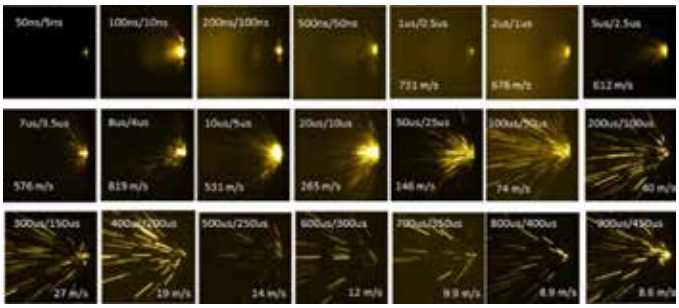
In this project, we aim to understand the physics and chemistry of laser ablation (LA) as it pertains to optical emission (laser-induced breakdown spectroscopy [LIBS]) and particle formation (LA inductively coupled plasma-mass spectrometry; LA-ICP-MS) with the goal of optimizing the performance of a combined sensor.

LIBS and LA-ICP-MS analytical techniques are routinely used for various applications; however, there is a lack of complete understanding of fundamental physics problems. A study such as this project is important for ultimately improving the analytical capabilities of both techniques and moving towards sensor fusion. We will address some of the long-lasting fundamental scientific questions important for LIBS and LA-ICP-MS sensors independently and will provide a base for developing an improved multimodal sensor with unique capabilities for both LIBS and LA-ICP-MS.

During FY 2015, a custom high vacuum chamber for laser ablation studies was designed and built, and is now operational. We also made significant progress in understanding molecular and particle formation mechanisms in laser ablation plumes. Our studies showed that the shock waves formed in the plume front are mediating the plasma chemistry leading to molecular formation. We prepared an article based on the results obtained during this study. In addition, preliminary experiments were performed for identifying the particle distribution generated from the laser ablation zone which is typically used as sample introduction in LA-ICP-MS. The particle ejection features were performed using DMA system, fast-gated imaging, and shadowgraphy.

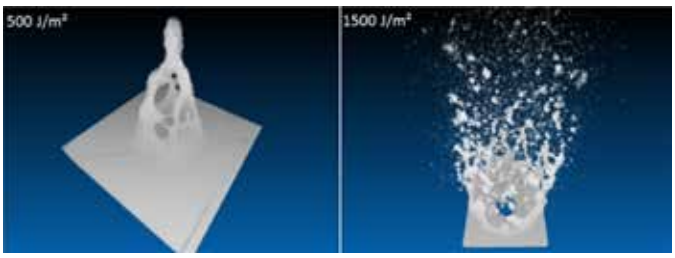


Spatio-temporal contour maps of excited Al and AlO species in an Al laser-produced plasma in air at atmospheric pressure levels.



Thermal radiation from particles ejected from a laser-produced graphite plasma at various times after the onset of plasma formation.

Also in FY 2015, molecular dynamics (MD) simulations of the non-equilibrium process of ultrafast laser-material interactions were studied at an atomic level, the results of which should lead to a better understanding of the nature and behavior of materials in a highly non-equilibrium state, microscopic mechanisms of melting, disintegration of material, formation of nano-clusters, and size distributions.



3D snapshots of fs LA plume expansion at 50 ps for two laser fluences.

Late in FY 2015 in collaboration with the University of Darmstadt and Purdue University, we investigated femtosecond (fs)-LA-ICP-MS as an analytical technique for determining the stoichiometry of thin films down to the nanometer scale. The use of fs-LA allows for the precise removal of material with high spatial and depth resolution that can be coupled to an ICP-MS to obtain elemental and isotopic information. Our results indicated that fs-LA-ICP-MS provides precise information of the thin film-substrate interface and also has the ability to detect the interdiffusion of cations.

The results obtained from FY 2015 showed significant insights into the molecular formation mechanisms during laser plasma expansion in a combustion medium like air. During FY 2016, these studies will be extended to different ambient mediums. The other continuing task is evaluating the particle size distribution and its direct correlation to initial plasma conditions.

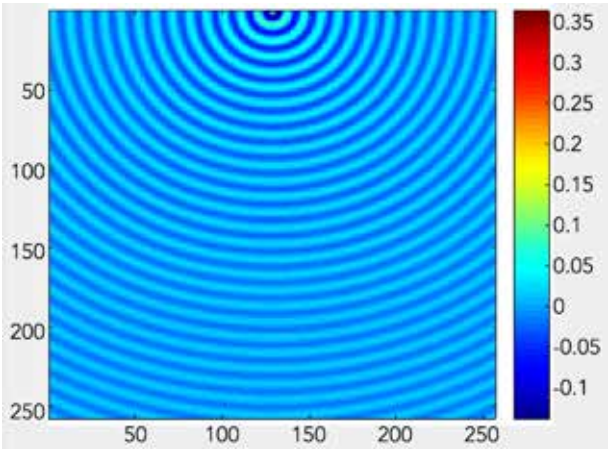
PN15012/2687

Modeling Underwater Sound in Coastal Environment to Accelerate Development of Renewable Ocean Energy

Wen Long

This project provides a cutting-edge modeling tool called FVSOUND for assessing the impacts of noise generated by the construction and maintenance of renewable ocean energy developments on marine mammals and fish in the coastal ocean.

The rapid growth of renewable energy from off-shore sources has raised concerns that underwater noise from construction and operation of off-shore devices may interfere with marine animal communication. Based on a finite volume method, an underwater sound model called FVSOUND is being developed to simulate sound propagation from marine-hydrokinetic energy devices or off-shore wind energy platforms. FVSOUND model accounts for four major mechanisms of ocean sound propagation to find the level away from sound sources: change of sound direction due to non-uniform distribution of ocean sound speed, reflection of sound from boundaries (surface, seabed, coastal lines), transmission of sound into the seabed, and attenuation. Prior models did not consider all mechanisms hence do not fit the requirements of sound assessment for coastal oceans. The current model is also built on a highly scalable, high performance parallel computing library with a fast numerical solution method, allowing us to provide sound levels quickly for any location within 50 miles of the noise source.



2D benchmark testing of radiation boundary for absorbing sound waves at the cut-off boundary. A sound source is placed on the top line of the figure. Colors indicate sound pressure relative to the sound source.

Sound transmission is closely related to ocean water density, which is in turn dependent on water temperature, salinity, and pressure (depth). Sound transmission in coastal waters is more temporally and spatially variable than in the open ocean due to seasonal influences of river plumes, the effect of meteorological wind stress and heat fluxes, and reflections of sound from complex coastal geometries. An advanced model can be used to account for this variability to predict sound fields accurately. However, coupled hydrodynamic and acoustic modeling has not been developed because the intensive computational resources needed for coupled modeling have not been readily available until recently.

Through this project, we have worked to improve the ability to predict sound propagation in coastal regions by providing two major innovations in the field of acoustic modeling. First, we formulated the acoustics problem mathematically for meeting the challenges of coupling time domain hydrodynamic model with frequency domain acoustic model. Second, we coupled of the well-known 3D ocean hydrodynamic circulation Finite Volume Community Ocean Model (FVCOM), which resolves the variations of water density and sea surface elevation, with the acoustic model that solves underwater sound transmission loss, reflection from lateral, bottom, and surface boundaries as well as refraction due to the varying density field.

Sound in coastal environment is complex due to several reasons: uneven distribution of sound speed due to rapid change of temperature and salinity across the domain, complex geometry from the coastal line and bathymetry, multiple reflections due to the coastal wedges, the transmission of sound into seabed, and attenuation of sound. Sound in a 3D domain is also challenging to solve because of the short sound wavelengths that indicate many grid points are required to resolve the sound field. This situation makes the number of unknowns in the resulting discretized equation system very large for moderately to high frequency sound. We found that our model FVSOUND is able to provide a solution to these issues accurately and quickly.

In FY 2016, we will finish the finite volume (triangular) grid implementation and produce the next version of the code. We will complete our field experiments in Sequim Bay, WA and will validate and polish the model for version 1.0 release.

PN15051/2726

Resolving the Reactor Neutrino Anomaly by Precision Beta Spectrometry

Kim A. Burns

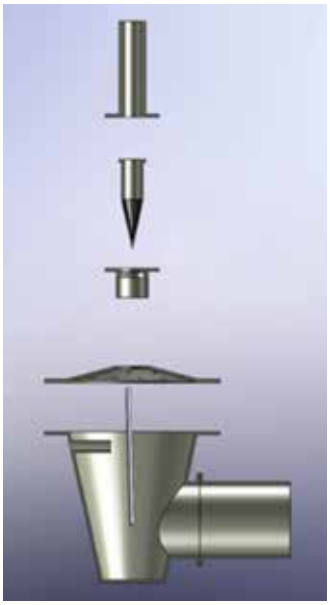
We are developing a new technique that will reduce the uncertainty associated the beta spectra and subsequent unfolded neutrino spectra.

The observed antineutrino rates at reactors that are vital to the study of neutrino oscillations are typically lower than model expectations. An experimental approach may provide a new understanding of neutrino physics to explain this deficit, though model estimation uncertainties may also play a role in the apparent discrepancy. Reactor neutrino spectra have been used in conjunction with neutrino detector measurements in the search for evidence of neutrino oscillations and in applications investigating nonproliferation surveillance methods. Next generation experiments aimed at measuring the last unknown mixing angle θ_{13} would also benefit from an accurate description of neutrino spectra. The absolute precision and the energy spectrum of the neutrinos released by fissions are the primary constraints in the interpretation of the reactor neutrino data.

Through the fission process, four isotopes ^{235}U, ^{239}Pu, ^{241}Pu, and ^{238}U contribute more than 99% of all reactor neutrinos with energies above the inverse beta decay threshold (neutrino energy ≥1.8 MeV). Reactor neutrino fluxes from the thermal fission of ^{235}U, ^{239}Pu, and ^{241}Pu are currently obtained by inverting measured total beta spectra obtained in the 1980s at a beam port at the High Flux Reactor of the Institut Laue-Langevin (ILL). The objective of this project is to design an experimental technique that promises reduced uncertainties for measured data using precision measurements of the beta energy spectrum from neutron induced fission using an accelerator.

A major advantage of an accelerator neutron source over a neutron beam from a thermal reactor like the one used at ILL is that the fast neutrons can be slowed or tailored to approximate various power reactor spectra. The ability to measure fission betas produced using a prototypic reactor spectrum provides two potential methods for quantifying the uncertainty with the existing measurements: quantifying the contribution from the ^{238}U fission betas and quantifying the difference between the reactor neutrino fluxes from the thermal fission and prototypic reactor fission of ^{235}U, ^{239}Pu, and ^{241}Pu.

In FY 2013, we completed a thorough literature search and completed a statistical analysis of the previous experimental setup and spectral unfolding methodology. Initial stages of an accelerator target design were completed to demonstrate the feasibility of completing a fission-based experiment using a proton accelerator. Preliminary results indicated that it is possible to generate an appropriate neutron spectrum and neutron flux to support the experiment. During FY 2014, the accelerator target design was completed, with material composition and layout of the target were determined based on nuclear physics, fabricability, mechanical requirements, and thermal analysis. We determined that the spectrometer would be a simple dipole with a time projection chamber to provide active tracking of the betas and ultimately a different set of systematic uncertainties compared to previous measurements.



Exploded view of fast spectra conceptual target configuration.

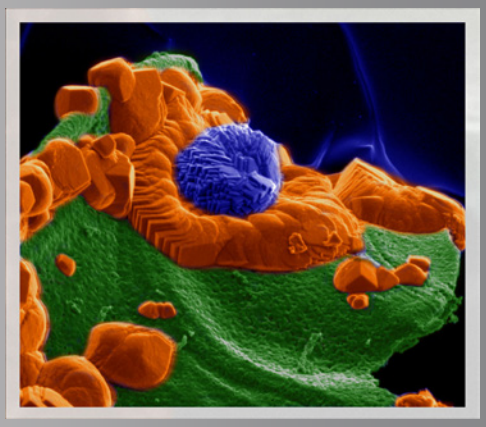
In FY 2015, alternative targets for the production of neutrons tailored to produce a range of different neutron spectra were investigated. In addition to applications associated with the reactor neutrino anomaly experiment, developing alternative tailored neutron spectra targets has many potential applications. Other potential missions for tailored neutron spectra include Cf-252 replacement, prototypic fast fission irradiation testing for fast reactor materials testing with high DPA rate, a standard neutron field for fissionable material detector development, nuclear data testing, neutron tomography systems for radiologic diagnostic imagining, and development of isotope production methods. The broad applicability of tailored neutron spectra represents a potential future funding avenue, but work will be required to define acceptable target configurations that produce a variety of neutron spectra.

PN13008/2489

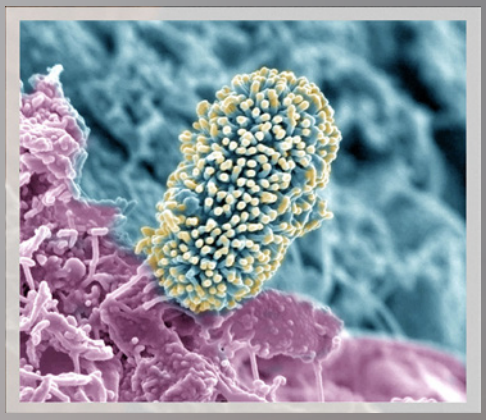
Additionally in FY 2015, the project focused on the design of two alternative targets, one producing a fast spectrum and the other a fusion spectrum. The design of a target to obtain a fast neutron spectrum was the natural evolution of the work performed on the PWR spectrum. For a fast spectrum design, the hydride moderator was removed, and the cooling system was changed to a liquid metal (Pb-Bi) eutectic mixture. The target material consisted of the same tungsten-rhenium alloy used for PWR applications. During operation, a beam of 30 MeV protons at 1 mA current was injected into the target. A tungsten reflector surrounded the irradiation chamber, in which a number of samples could be placed in a circular pattern. Based on neutron escape and capture events, current results indicated an estimated neutron yield of 1.0E14 n/s for the fast neutron target.

The design of an effective neutron source for fusion applications presented a number of challenges. Neutron emission should occur ideally in a narrow-band region around 14 MeV, corresponding to neutrons generated by a D-T fusion reaction. In addition, an intense neutron flux should be produced in this energy range. To obtain these characteristics, it would be necessary to select a different material for the target. Research was conducted in this area, in particular looking at quasi-monochromatic neutrons emitted by ^{7}Li(p,n) reaction. Proton interactions with a lithium target in the energy range targeted below 30 MeV present a quasi-monochromatic emission of neutrons above 10 MeV with a peak around 14 MeV, depending on the energy of the incoming protons. Final geometric configurations were not completed prior to the conclusion of FY 2015 due to the identification of potential material compatibility issues.

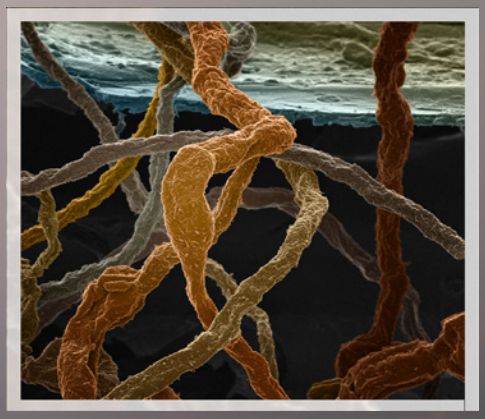
ON THE COVER:



Down deep underground, the reaction between the mineral forsterite (green object in image) and CO_2 results in the formation of a different mineral, siderite (orange and blue)—which effectively captures the CO_2 in a solid stable form. The discovery by researchers at PNNL paints a clearer picture of what happens when greenhouse gas emissions are injected in the subsurface and helps inform capture and storage strategies. DOE's Office of Basic Energy Sciences funded the research, which was conducted at EMSL. The image was captured with a scanning electron microscope.



A soil bacterium's captivating appendages reflect the magic of the rhizosphere, or the plant root zone, which is highly influential and impacts many environmental processes. Through an EMSL research campaign, scientists at EMSL, PNNL, and the University of Missouri are studying the role and impact of microbial communities in the rhizosphere using multiple capabilities. The work is specifically focused on understanding how carbon allocation to the root environment impacts the diversity and size of the rhizosphere community. This image was captured using a dual-beam focused ion beam/scanning electron microscope at EMSL. The research was funded by the DOE BER.



The fungus *Trichoderma reesei*, shown here extending its thread-like filaments on corn stover, could be a key to quick and efficient conversion of biomass to fuels. The fungus is known for its prolific production of biomass-chomping enzymes.Researchers at PNNL have studied the genomes of *Trichoderma reesei* and other fungi, seeking to better understand how the enzymes are produced and can be applied to achieve breakthroughs in biofuel production. This image was captured by scientists at EMSL. The research was funded by the DOE BER.

2015 Annual Report

Laboratory Directed Research & Development

www.pnnl.gov

Pacific Northwest
NATIONAL LABORATORY

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

U.S. DEPARTMENT OF
ENERGY

PNNL-25278