Idaho National Laboratory **ANNUAL REPORT FY2012**

LDRD PROJECT SUMMARIES

iNL Idaho National Laboratory

CONTENTS

NUCLEAR SCIENCE & TECHNOLOGY

NATIONAL & HOMELAND SECURITY

ENERGY & ENVIRONMENT SCIENCE & TECHNOLOGY

INSTITUTE FOR NUCLEAR ENERGY SCIENCE & TECHNOLOGY

CENTER FOR ADVANCED ENERGY STUDIES

CENTER FOR ADVANCED MODELING & SIMULATION

INSTRUMENTATION, CONTROL AND INTELLIGENT SYSTEMS

APPENDICES

NUCLEAR
SCIENCE
AND TECHNOLOGY

Neptunium Redox Chemistry in Irradiated Aqueous Nitric Acid

Bruce J. Mincher and Alena Paulenova[1]
10-001

The reliable extraction of actinides from nuclear fuel dissolution—a requirement of an advanced nuclear fuel cycle—requires the selection and maintenance of an appropriate oxidation state. Neptunium is especially problematic in this regard, as NpIV and NpVI are extractable with the common fuel cycle ligands, while NpV is not. Further, in irradiated solution neptunium valence state changes result in a mixture of these oxidation states, resulting in unreliable separations under process conditions. Research into the parameters that control neptunium redox speciation is underway worldwide, yet no research group has investigated the effect of radiation. Therefore, we irradiated neptunium solutions of known speciation using a 12,000 Ci ^{60}Co source, and measured the changes in speciation using a Cary 6000 UV/Vis spectrophotometer. Rates of valence state changes versus absorbed radiation dose were measured, and speciation was found to depend on the radiolytic generation of oxidizing free radical species and reducing nitrous acid. We successfully simulated the experimental results using a kinetic model composed of the known radiolysis reactions for water and nitric acid.

Summary

We discovered that in the initial stages of irradiation neptunium is oxidized to extractable NpVI by oxidizing radiolysis products such as •OH and •NO_3 radicals. These short-lived species are produced by the radiolytic decomposition of water and nitric acid. As irradiation continues the longer-lived radiolysis product nitrous acid accumulates in solution, and the system becomes reducing with respect to neptunium. Neptunium is then converted to inextractable NpV. The radiolytic production of NpV, NpVI, and nitrous acid were measured spectrophotometrically, and depend on the absorbed gamma-dose to the solution and the concentration of nitric acid, which is itself oxidizing toward neptunium. NeptuniumIV was not produced in our experiments. An example of the change in redox speciation versus absorbed dose is shown in Figure 1, for a 4 M nitric acid solution containing 6 mM total neptunium.
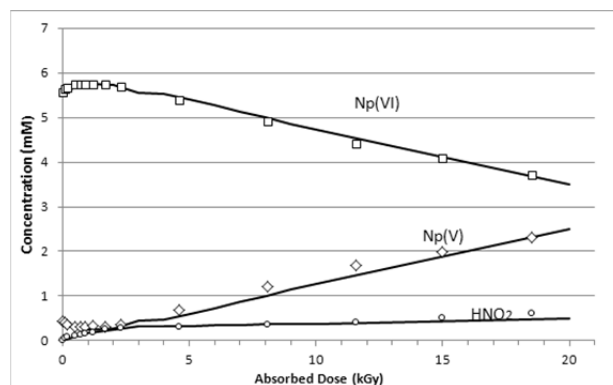
FIGURE 1. The initial oxidation of 6 mM total neptunium by free radical radiolysis products, followed by the reduction of neptunium by radiolytically-produced nitrous acid in irradiated 4 M nitric acid solution.

We successfully modeled this behavior using a kinetic model containing the radiolysis reactions for water and nitric acid, and the known rate constants for the reactions of the major radical species with neptunium. The data points shown in Figure 1 are the measured absorbance values for NpV at 980nm, NpVI at 1225 nm and HNO_2 at 254 nm. The curves in Figure 1 show the modeled fit to the data.

This program has contributed to the development of a state-of-the-art radiation chemistry capability at INL, since this is the first project that has investigated the effect of radiation on metal redox chemistry. The project also resulted in the granting of a Ph.D. degree to Martin Precek at Oregon State University, under the direction of co-PI Professor Alena Paulenova.

Benefits to DOE

The results of this work directly benefit the optimization of an advanced fuel cycle, in which reliable partitioning of neptunium from dissolved nuclear fuel is required. Whether the final fuel cycle scheme relies on neptunium co-extraction, or neptunium partitioning, reliable maintenance of the selected neptunium species will be necessary.

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[1] Oregon State University

Relevant Publications and Presentations

Mincher, B.J., M. Precek, S.P. Mezyk, L.R. Martin, and A. Paulenova, "The Role of Oxidizing Radicals in Neptunium Speciation in γ-irradiated Nitric Acid," *J Radioanal Nucl Chem*, in press DOI 10.1007/s10967-012-1937-1, 2012.

Mincher, B.J., M. Precek, M.G. Elias, S.P. Mezyk, and A. Paulenova, "The Redox Chemistry of Neptunium in γ-irradiated Aqueous Nitric Acid," *Radiochim Acta.* (accepted)

Mincher, B.J., "Irradiation Effects on Neptunium Oxidation States," *Proceedings of the first ACSEPT International Workshop, Lisbon, Portugal, March 31–April 2, 2010.*

Precek, M., B.J. Mincher, and A. Paulenova, "Interactions of Nitrous Acid with Neptunium in Nitric Acid Solutions," *35th Actinide Separations Conference, Charlotte, NC, May 23–26, 2011.*

Mincher, B.J., "Redox Chemistry of Neptunium in Irradiated Nitric Acid," *Methods and Applications of Radioanalytical Chemistry; MARC IX, Kailua Kona, HI, March 20–25, 2012.*

Precek, M., A. Paulenova, and B.J. Mincher, "Reduction of Np(VI) in Irradiated Solutions of Nitric Acid," *ATALANTE 2012 - Nuclear Chemistry for Sustainable Fuel Cycles conference, Le Corum Montpellier, France, September 2–7, 2012.*

Ultrasonic Transducer Sensors for In-Pile Detection of Dimensional Changes

Steven Taylor, Joy Rempe, and Bernhard Tittman[1]
10-007

At INL's ATR, deformation of specimens due to irradiation is currently evaluated out-of-pile, where the properties of materials are measured after the specimens have been irradiated for a specified length of time. The time and labor to remove, examine, and return irradiated specimens for each measurement makes the current out-of-pile approach very expensive. In addition, the out-of-pile measurements only capture the specimen's end state after it is removed from the reactor. Therefore, data are not obtained under prototypic conditions, and removal and examination processes may disturb the phenomena of interest. Although linear variable differential transducers have been successfully deployed at other test reactors and are being investigated for ATR applications, ultrasonic transducers offer the potential for a more compact, higher temperature, more accurate, and multi-dimensional real-time sensor for detecting geometry changes of creep specimens during irradiation. This three-year project investigated the feasibility of using ultrasonic methods for in-pile measurement of geometry changes in creep specimens of candidate new reactor materials during irradiation testing.

Summary

In this project, laboratory evaluations were completed at INL and at Pennsylvania State University to optimize components required for using ultrasonic techniques for in-pile elongation measurements. Key components of an in-pile setup initially investigated (see Figure 1a) include a magnetostrictive transducer (e.g., a driver coil with magnetostrictive core), a Remendur guide, a coupling between the Remendur guide and a long stainless steel wave guide that allowed the transducer to be located outside of the reactor, and a creep specimen with an acoustic horn to optimize the signal.

Laboratory evaluations identified several options that would eliminate unwanted reflections in this initial setup, such as: (1) significant reductions in the length of the stainless steel waveguide, (2) elimination of brass coupling between Remendur and stainless steel waveguides, (3) replacement of the acoustic horn on the creep specimen with an acoustically-clean "button," (4) optimization of the magnetostrictive transducers, and (5) elimination of acoustic reflections from the end of the Remendur waveguide. The "buttons" that were found to be superior to acoustic horns were similar to conventional butt-end shoulders used in tensile testing, except the buttons were designed to slide onto the specimen. Attachment methods were developed to ensure that the buttons could impart the desired tensile load and be easily attached without concerns about perfect specimen-to-button alignment. As illustrated in Figure 1(b), these buttons were found to be very effective at eliminating unwanted reflections, especially when implemented in conjunction with other enhancements identified in this effort.

This effort also funded a Pennsylvania State University graduate student to complete his doctoral thesis.

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[1] Pennsylvania State University

(a)

(b)

(a)

(b)
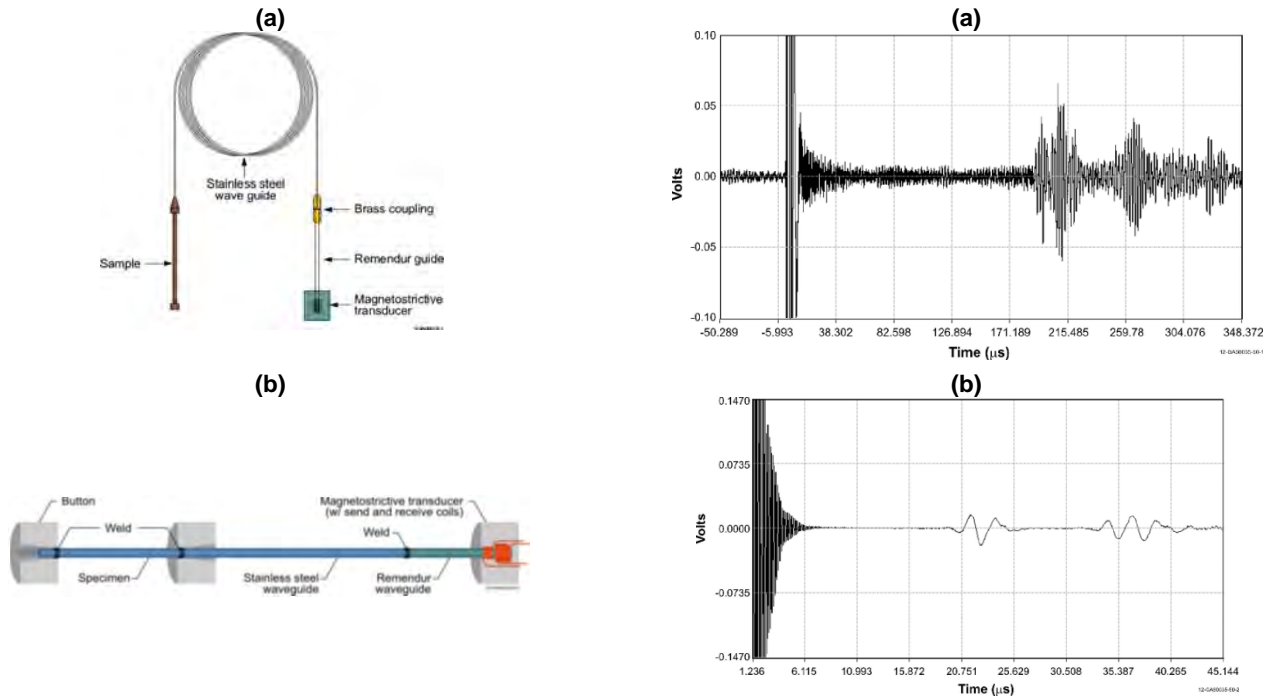
FIGURE 1. Representative system components and typical pulse/echo results using: (a) initial concept with an acoustic horn; and (b) enhanced concept with buttons.

Benefits to DOE

Techniques investigated in this project support the DOE energy security mission by developing and demonstrating high-temperature in-pile sensors benefitting DOE-NE. This research enhances INL's expertise for producing optimized, more reliable, and more compact in-pile instrumentation. Enhanced instrumentation from this research can also increase testing capabilities of INL's ATR, which benefits various U.S. programs that conduct testing at this unique facility.

Relevant Publications and Presentations

Rempe, J.L., D.L., Knudson, J.E. Daw, T. Unruh, B. Chase, and K. Davis, "Enhanced In-pile Instrumentation at the Advanced Test Reactor," *invited paper for ANIMMA 2011 Special Edition, IEEE Transactions on Nuclear Science*, MS # SCH-TNS-00196-2011, accepted September 27, 2011.

Rempe, J.L., M.K. Meyer, D.L. Knudson, K.G. Condie, J.E. Daw, and S.C. Wilkins, "ATR NSUF Instrumentation Enhancement Efforts," Invited paper, *NPIC HMIT Special Edition, Nuclear Technology,* Vol. 173, 66–77, January 2011.

Kim, B.G., J.L. Rempe, J.F. Villard, and S. Solstad, "Review of Instrumentation for Irradiation Testing of Fuels and Materials," *invited review paper, Nuclear Technology,* Vol.176, 155–187, November 2011.

Guers, M.J., "In-situ Monitoring of Remote Specimens Using Ultrasonic Guided Waves," Pennsylvania State University, Ph.D. Dissertation, 2011.

Kim, B.G., J.L. Rempe, D.L. Knudson, K.G. Condie, and B.H. Sencer, "Development of an In-situ Creep Testing Capability for the Advanced Test Reactor," *7th International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human Machine Interface Technologies (NPIC&HMIT 2010), Las Vegas, NV, November 7–11, 2010.*

Knudson, D.L. and J.L. Rempe, "Recommendations for Use of LVDTs in ATR High Temperature Irradiation Testing," *7th International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human Machine Interface Technologies (NPIC&HMIT 2010)*, *Las Vegas, NV, November 7–11, 2010.*

Rempe, J.L., D.L. Knudson, K.G. Condie, J.E. Daw, H. Ban, B.S. Fox, and G.E. Kohse, "New Sensors for the Advanced Test Reactor National Scientific User Facility," *Invited paper for ANIMMA Special Edition, IEEE Transactions on Nuclear Science*, Vol. 57, 2653-2661, October 2010.

Rempe, J.L., D.L. Knudson, J.E. Daw, T. Unruh, B. Chase, K. Davis, R. Schley, and S. Taylor, " New Sensors for Irradiation Testing at Materials and Test Reactors," *IAEA Technical Meeting on In-Pile Testing and Instrumentation for Development of Generation-IV Fuels and Materials, August 21-24, 2012, Halden, Norway.*

Rempe, J.L., D.L. Knudson, J.E. Daw, T. Unruh, B. Chase, K. Davis, R. Schley, and S. Taylor, "New Instrumentation for Irradiation Testing in High Flux Materials and Test Reactors," *8th International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human Machine Interface Technologies (NPIC&HMIT 2012), San Diego, CA, July 22-26, 2012.*

Rempe, J.L., J.E. Daw, D.L. Knudson, R. Schley, and L. Bond, "FCRD In-Pile Instrumentation Development," *Panel Discussion at the ANS 2011 Annual Meeting*, *Hollywood, FL, June 28, 2011.*

Daw, J.E., J.L. Rempe, R.S. Schley, K.B. Boudreau, and G. Kohse, "Instrumentation to Enhance ATR NSUF Irradiation Testing," *Advanced Test Reactor National Scientific User Facility User's Week*, June 9, 2011.

Rempe, J.L., B.G. Kim, G.E. Kohse, S. Solstad, and J.F. Villard, "Current Instrumentation to Support FC R&D Irradiations," *FCRD In-Pile Instrumentation Workshop, Las Vegas, Nevada, November 10, 2010.*

Rempe, J.L., "Challenges of In-Pile Sensing and Transmission," *NanoNuclear Workshop, Washington, DC, September 13-15, 2010.*

Rempe, J.L. and G.E. Kohse, "In-core Instrumentation: Motivation, Approaches, and Examples," *ATR NSUF 2010 User's Week, Experimenter's Course on Instrumentation, Idaho Falls, ID, June 8, 2010.*

Rempe, J.L., "LDRDs to Enhance ATR NSUF Instrumentation," *ATR NSUF Scientific Review Board Meeting, Idaho Falls, ID, June 7, 2010.*

Rempe, J.L., "In-pile Instrumentation for the ATR," *Nuclear Engineering Colloquium, Pennsylvania State University, State College, Pennsylvania, April 22, 2010.*

Daw, J.E. and J.L. Rempe, "New Sensors for Advanced Test Reactor Irradiations," *INL ATR NSUF ATR Workshop on Irradiation Testing and Planning, ANS Student Meeting,* Georgia Institute of Technology, *Atlanta, GA, April 14, 2010.*

Rempe, J.L., "In-pile Instrumentation for ATR NSUF Irradiations," *INL ATR NSUF ATR Workshop on Irradiation Testing and Planning, ANS Student Meeting, University of Michigan, Ann Arbor, Michigan, April 8, 2010.*

Rempe, J.L., "New Sensors for Advanced Test Reactor Irradiations," *ATR NSUF Industry Advisory Committee, Palo Alto, California, February 9, 2010.*

Multiscale Modeling and Simulation of Nuclear Fuel Performance

Rich Williamson, Derek Gaston, Michael Tonks, and Cody Permann
10-017

Current state-of-the-art computational tools used to simulate nuclear fuel performance employ highly empirical models, which prohibit application to new fuel materials and designs, or extended fuel burnup. These tools are further restricted to 1.5 or 2-D geometries, prohibiting analysis of important 3-D behavior, and are limited to use on a single computer, limiting applications to simple problems. The major objective of this project was to develop a multiscale 3-D fuel performance capability that fully couples a mesoscale description of the nuclear fuel microstructural evolution with an engineering-scale prediction of fuel behavior, resulting in a simulation capability that is truly predictive. Additional objectives included ensuring the computational tool ran efficiently on massively parallel computers, that it contained accurate nonlinear material and behavioral models, and that it included intelligent adaptive time-step control.

Summary

The general MOOSE computational framework has been under development at INL since 2008, and MOOSE was used as the basis of INL's engineering scale fuel performance code, BISON. Under this project, the mesoscale fuels code MARMOT was developed using the MOOSE framework, and MARMOT and BISON were coupled to create MOOSE/BISON/MARMOT (MBM), a powerful multiscale, parallel, 2-D and 3-D fuel simulation capability. Additional development over the duration of the project included: (1) enhancements to MOOSE to permit efficient application on massively parallel computing systems, (2) development of highly nonlinear plasticity and creep models within the MOOSE Jacobian Free Newton Krylov numerical scheme, (3) development of an intelligent adaptive time step control algorithm applicable to complex steady and transient reactor operation, and (4) the initial implementation and demonstration of mechanical contact with friction. These development efforts have been largely documented in several journal articles.

The parallel computational capability of MOOSE/BISON was demonstrated by simulating the behavior of a highly resolved full-length discrete-pellet fuel rod. This fully-coupled implicit simulation required over 234 million degrees of freedom and was run on the INL FISSION high performance computer, using up to 12,000 processors. The parallel capability of MARMOT was investigated on a large polycrystal simulation, using up to 8,000 processors.

Results obtained from these exercises demonstrated good strong and weak scaling for thousands of processors, demonstrating that the MBM codes are applicable to and can be efficiently used to solve very large problems.

Results from two MBM applications are shown in Figures 1 and 2. For the first, BISON was used to study the effects of a manufacturing fuel defect known as a Missing Pellet Surface (MPS). Figure 1 shows BISON predicted fuel temperature and cladding stress in a light water reactor rodlet containing five fuel pellets. Note that the middle pellet is missing a portion of its outer surface, resulting in a large gas gap and much higher local fuel temperatures. Stress and deformation in the cladding adjacent to the missing pellet surface is significantly increased and can result in fuel rod failure. Nonlinear creep deformation models developed as part of this project were essential in accurately simulating this behavior. Significantly, this is the first time MPS behavior has been analyzed in 3-D over the full life of the fuel rod.
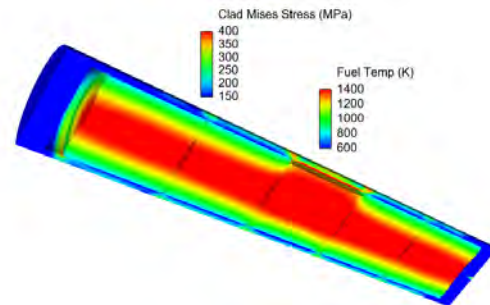
FIGURE 1. Temperature and stress results from a MOOSE/BISON nonlinear analysis of a fuel rod containing a defective fuel pellet.

The second example is a coupled BISON/MARMOT simulation where we coupled four 2-D MARMOT simulations of void nucleation and growth to a 2-D axisymmetric BISON simulation of a five pellet rodlet. During the simulation, the macroscale temperature and neutron flux were passed to the four MARMOT simulations at each time step, and the microstructure was then evolved and used to determine the effective thermal conductivity. This conductivity was passed back to BISON for use in the macroscale thermomechanics equations. This simulation demonstrates the direct coupling between MARMOT and BISON, providing a significantly more predictive modeling capability.
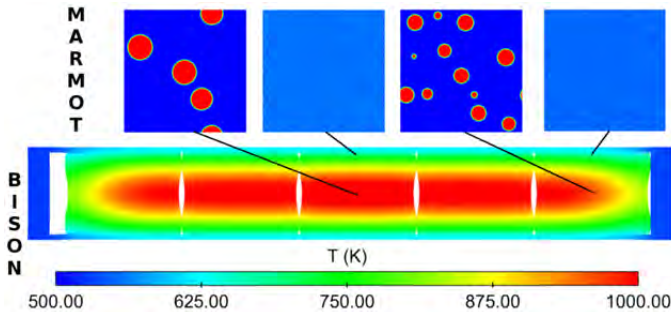
FIGURE 2. Example of concurrent coupling between MARMOT and BISON, in which four 2-D MARMOT simulations of void nucleation and growth are coupled to a 2-D axisymmetric BISON simulation of a five pellet rodlet. Temperature and neutron flux are passed down to the MARMOT simulations and the effective thermal conductivity is passed back up to BISON.

Benefits to DOE

The MBM computational tools have been selected as the Nuclear Energy Advanced Modeling and Simulation code platform for fuel rods and lower length-scale phenomena with recent simulations used to investigate novel accident tolerant fuel design. The Consortium for Advanced Simulation of Light Water Reactors is leveraging MBM to support the Materials Performance and Optimization focus area for pellet clad interaction. BISON is being leveraged for supporting analysis and experimental design for the Fuel Cycle Research and Design campaign (including future ATR experiments) and to investigate novel clad materials for the Light Water Reactor Sustainability program. BISON has recently been applied to plate fuel designs in support of the Reduced Enrichment for Research and Test Reactors program.

Relevant Publications and Presentations

Williamson, R.L., J.D. Hales, S.R. Novascone, M.R. Tonks, D.R. Gaston, C.J. Permann, D. Andrs, and R.C. Martineau, "Multidimensional Multiphysics Simulation of Nuclear Fuel Behavior," *Journal of Nuclear Materials*, Vol. 423, 149, 2012.

Tonks, M.R., D.R. Gaston, P.C. Millet, D. Andrs, and P. Talbot, "An Object-Oriented Finite Element Framework for Multiphysics Phase Field Simulations," *Computational Materials Science*, Vol. 51, 20, 2012.

Hales, J.D., S.R. Novascone, R.L. Williamson, D.R. Gaston, and M.R. Tonks, "Solving Nonlinear Solid Mechanics Problems with the Jacobian-Free Newton Krylov Method," *Computer Modeling in Engineering and Sciences*, Vol. 84, 123, 2012.

Gaston, D.R., L. Guo, G. Hansen, H. Huang, R. Johnson, H. Park, R. Podgorney, M.R. Tonks, and R.L. Williamson, "Parallel Algorithms and Software for Nuclear, Energy, and Environmental Applications. Part I: Multiphysics Algorithms," *Comm. in Computational Physics*, Vol. 12, 807, 2012.

Gaston, D.R., L. Guo, G. Hansen, H. Huang, R. Johnson, H. Park, R. Podgorney, M.R. Tonks, and R.L. Williamson, "Parallel Algorithms and Software for Nuclear, Energy, and Environmental Applications. Part II: Multiphysics Software," *Comm. in Computational Physics*, Vol. 12, 834, 2012.

Tonks, M.R., P. Millett, P. Nerikar, D. Andersson, C. Stanek, D.R. Gaston, D. Andrs, and R.L. Williamson, "Multiscale Simulation of Heat Conduction in UO$_2$ Fuel," *Journal of Nuclear Materials* (2012). (submitted)

Chockalingam, K., P.C. Millett, and M.R. Tonks, "Effects of Intergranular Gas Bubbles on Thermal Conductivity," *Journal of Nuclear Materials*, Vol. 430, 166, 2012.

Zhang, L., M.R. Tonks, P.C. Millett, Y. Zhang, K. Chockalingam, and S.B. Biner, "Phase-Field Modeling of Temperature Gradient Driven Pore Migration Coupling With Thermal Conduction," *Computational Materials Science*, Vol. 56, 161, 2012.

Millett, P.C. and M.R. Tonks, "Meso-scale Modeling of the Influence of Intergranular Gas Bubbles on Effective Thermal Conductivity," *Journal of Nuclear Materials, Vol.* 412, 281, 2011.

Tonks, M.R., D.R. Gaston, C. Permann, P.C. Millet, G. Hansen, and D. Wolf, "A Coupling Methodology for Mesoscale-informed Nuclear Fuel Performance Codes," *Nuclear Engineering and Design*, Vol. 240, 2877, 2010.

Spencer, B.W., J.D. Hales, S.R. Novascone, and R.L. Williamson, "3D Simulation of Missing Pellet Surface Defects in Light Water Reactor Fuel Rods," *Proceedings of TopFuel 2012, Manchester, UK, September 2012.*

Tonks, M.R., D.R. Gaston, P.C. Millett, D.A. Andersson, and C. Stanek "Multiscale Fuel Performance Modeling: Coupling Atomic, Meso and Continuum Level Simulations," *American Nuclear Society General Meeting, Chicago, IL, June 2012.*

Tonks, M.R., D.R. Gaston, P.C. Millett, C. Permann, and D. Andrs, "An Object-Oriented Finite Element Framework for Multiphysics Phase Field Simulations," *SIAM Conference on Parallel Processing for Scientific Computing, Savannah, GA, February 2012.*

Tonks, M.R., D.R. Gaston, P.C. Millett, P. Nerikar, D.A. Andersson, and C. Stanek, "Advanced Multiscale Fuel Performance Modeling," *Global 2011, Makuhari, Chiba, Japan, December 2011.*

Hales, J., D. Andrs, D.R. Gaston, S. Novascone, C. Permann, M.R. Tonks, and R.L. Williamson, "Fully Coupled, 3D, Multi-physics for Analysis of Nuclear Fuel," *11th US National Congress on Computational Mechanics, Minneapolis, MN, 2011.*

Tonks, M.R., D.R. Gaston, D. Andrs, C. Permann, R.L. Williamson, J. Hales, S. Novascone, P.C. Millett, B. Biner, C. Stanek, D. Andersson, and P. Nerikar, "Advanced Multiscale Fuel Performance Modeling," *Materials Modeling and Simulation of Nuclear Fuel Workshop, Aix En Provence, France, September 2011.*

In-Pile Temperature Monitor and Control for ATR

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10-022

The advantages of using a fiber-optic temperature sensor include: small size, high sensitivity, reliability, and the lack of signal interference from electric and magnetic fields. It is well known that irradiation temperature is one of the most critical parameters that have a strong impact to the microstructural development under irradiation. INL's ATR plays a significant role in nuclear materials and fuel development programs through in-pile irradiation experiments. The purpose of this project is to develop a fiber-optic-based temperature sensor for real time in-pile measurement. The capability to record in-pile irradiation temperatures is essential to the success and the quality of ATR irradiation experiments. Our goal is to develop a prototype fiber-optic temperature sensor to measure and record the irradiation temperature for the materials and fuels irradiation tests in a research and test reactor that will significantly improve the quality of irradiation test data by providing the real time temperature measurement and temperature history during irradiation.

Summary

A major accomplishment for this project was the successful demonstration of a fiber-optic sensor yielding extremely high resolution (0.01°C) temperature measurement over a dynamic range (room temperature to 800°C). The upper temperature limit of this sensor is only restricted by the silica fiber material used for the sensor fabrication. This upper temperature limit can be increased by using sapphire fiber instead of silica fiber. Note that the current temperature range is adequate for most of the metallic materials irradiation experiments in ATR. We have evaluated different sensor configurations from this work and identified that the best option is a 4- to 5-mm-long, 0.80-mm-diameter ceramic expansion tube with a single mode silica fiber and superluminescent diode light source. We also demonstrated that a single measurement system can support multiple sensors with up to 16 different temperature sensors in an experiment.

The advantages of using the current sensor are its simple configuration, low cost, high resolution, and dynamic temperature range (room temperature to 800°C). Significant effort has been focused on the data processing algorithm to obtain real-time reliable and accurate temperature measurement automatically. One of the

challenges we discovered is the measurement system's response to an unexpected interruption, such as a power outage or computer malfunction (i.e., operating system crash). This is critical for temperature measurement of an ATR irradiation experiment, which has an irradiation cycle of typically ~50 days. The algorithm developed from this work can quickly recover the temperature measurement from any interruption point within ~1°C of the actual temperature.

We also performed a long-term, high-temperature stability experiment. The fiber optic sensor was kept at 760°C for 50 days. The temperature reading from the sensor drifted about 5°C with a rate of approximately 0.1°C/day. We believe that this temperature drift can be further reduced by improvement on sensor fabrication and processing. As a final product of this three-year LDRD project, three prototype fiber-optic sensors (each with a 20-m-long fiber-optic cable) are to be ready for an ATR irradiation experiment.

Benefits to DOE

R&D on this sensor is important to INL's nuclear fuel and materials irradiation testing mission. It can significantly improve the ATR NSUF program for the nation by providing high quality irradiation test data with reliable temperature measurement, which is currently unavailable due to high costs and space limitation in the core. The fiber-optic temperature measurement system developed by our collaborator at The University of Houston is critical to test and fabricate sensors with different designs. Once the sensor is demonstrated in an ATR irradiation experiment, this type of fiber-optic temperature sensor will find its application for the mission in other federal agencies, such as the U.S. Department of Defense where nuclear power is frequently used. We submitted an Invention Disclosure.

Relevant Publications and Presentations

Zhihua, S., J. Gan, Q. Yu, Q. Zhang, Z. Liu, and J. Bao, "High-resolution Fiber Optic Temperature Sensors Utilizing Broadband Infrared Superluminescent Diode and Novel Spectral Curve Fitting Technique." (submitted)

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[1] University of Houston

Reversible Gas Phase Reactions for Recovery of Graphite from Recycled HTGR TRISO Fuel

Scott Herbst, Mitchell Greenhalgh, and Jerry Christian
10-026

High Temperature Gas Reactor (HTGR) concepts will use nuclear fuels containing tristructural isotropic (TRISO) coated fuel particles embedded in carbonaceous fuel compact material. The spherical TRISO particles are 0.5-1 mm in diameter and consist of a central kernel of the nuclear reactor fuel (uranium dioxide [UO_2] or uranium oxycarbide [UCO]), surrounded by successive layers of low density porous carbon buffer, dense inner pyrolytic carbon (PyC), silicon carbide (SiC), and dense outer PyC, as depicted in Figure 1. This project examined recovering the carbon from these graphite fuels, including radioactive carbon-14 (C-14) from bulk graphite, as an alternative, and improvement to burning the carbon to CO_2 in air or oxygen with subsequent release to the environment. The carbon recovery step would form the basis for the headend processing of used HTGR fuels to recover valuable uranium and irradiation products. In this scenario, the carbonaceous layers would be removed and captured through recycling the reactive gas while the exposed fuel kernel could be subsequently processed using conventional techniques. C-14 would be selectively removed from the bulk graphite, enabling the graphite to be disposed of as a low-level waste. Reaction kinetics are being experimentally determined with surrogate TRISO particles and several reactive gases, including sulfur (S), fluorine (F_2), nitrogen trifluoride (NF_3), chlorine (Cl_2), and hydrogen (H_2), to establish practicality of these processes. Each reactant gas is predicted to react with the different carbon containing layers to form carbon-containing gaseous compounds that can be reversibly dissociated back into carbon and reactant gas. The results of the tests will be used to derive mass balance and throughput rates with the various gases for treatment of the HTGR fuels.
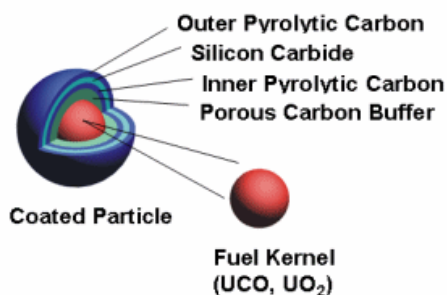
FIGURE 1. Structure of a typical TRISO fuel particle (www.nextgenerationnuclearplant.com/i/triso.gif).

Summary

A Thermal Gravimetric Analyzer (TGA) instrument was used to perform reaction rate evaluations on the TRISO particle layers with each of the reaction gases previously listed. Results of these experiments showed that no reaction was observed with either the PyC or SiC layers in S, H_2, or Cl_2 gases, although they are predicted thermodynamically to occur. The decomposition of carbon disulfide (CS_2, the reaction product of carbon with sulfur) was also investigated in the temperature range between 275°C and 400°C. The results indicate that CS_2 will not reversibly decompose, as predicted thermodynamically, at a practical rate. However, reaction rates for the PYC and SiC layers were observed in both the NF_3 and F_2 experiments and consequently we focused on these systems.

Both F_2 and NF_3 provide a source of fluorine to react with the carbon layers. However, NF_3 is considered less toxic, less corrosive, and less reactive at ambient temperature than F_2 gas. Consequently, NF_3 would be more easily handled during transport, storage, and processing operations than F_2 gas. Therefore, we compared the reaction rates of these two gases with the different carbonaceous TRISO layers. Nickel and quartz glass were evaluated as materials of construction for both the sample holders and balance wires in the TGA instrument with F_2 as a function of reaction temperature. Nickel was found to be resilient to fluorine at temperatures at or below ~600°C provided the sample holder and wire were passivated at elevated temperatures with fluorine gas prior to use. The quartz reaction chamber reacted with the gases and was replaced with alumina which proved to be nonreactive in the system. The obtained data indicate that the SiC layer is sufficiently reactive with either F_2 at 400°C or NF_3 at 500°C to be potentially useful for the removal of the SiC layer. This reaction can be conducted with nickel materials of construction at these temperatures. The NF_3 and F_2 are not reactive enough with the outer or inner pyrolytic carbon layers of the TRISO particles at temperatures below about 650°C to be practical.

In addition to TRISO particles, bulk graphite reactions in NF_3 were performed in an effort to demonstrate the selective removal of the C-14 from the surface of irradiated graphite utilized in HTGR systems. The optimal test conditions were determined using graphite that had not been irradiated and two tests on irradiated graphite

were performed utilizing these conditions. The acquired data demonstrated that C-14 and tritium can be selectively removed from irradiated graphite samples with NF_3 gas and captured in basic sodium hydroxide and nitric acid scrub solutions, respectively.

Benefits to DOE

The ability to process irradiated HTGR fuels and recover valuable uranium and fission products is an important aspect of future nuclear fuel cycles. Nuclear fuels based on TRISO particles contain a SiC layer that is very inert (nonreactive) by design, purposely keeping the irradiation products and fuel contained inside the kernel of the fuel particles. An efficient, cost-effective method of removing the SiC layer and also C-14 from the bulk graphite is important to the success of future fuel cycles based on the HTGR and TRISO particles. This need has also been expressed by cognizant industry experts. The reaction of TRISO particle layers and bulk graphite with F_2 or NF_3 is a potential method to fill this gap.

Relevant Publications and Presentations

A peer-reviewed publication comparing the reaction rates of pyrolytic carbon and SiC with NF_3 and F_2 gases is currently in preparation.

Comprehensive Thermodynamic Models for Aqueous Partitioning of Actinides from Used Nuclear Fuel

Peter Zalupski and Simon Clegg[1]

10-027

Proper consideration of non-ideal solution chemistry in aqueous electrolyte and non-aqueous solute mixtures is necessary when considering the operation of liquid-liquid distribution equilibria involved in used nuclear fuel separations. Quantitative description of chemical interactions in complex liquid phases may be realized through the process of thermodynamic parameterization of theoretically represented mixtures. The construction of such thermodynamic models allows for numerical representation of non-ideal solute behavior in aqueous and organic phase components of a liquid-liquid distribution. Ultimately, the construction of such theoretical models supports predictive modeling activities focused on the identification of correct equilibrium sets that control the liquid-liquid process.

The development of the thermodynamic model for the aqueous electrolyte system: $Eu^{3+}/H^+/Na^+/NO_3-/H_2Mal/HMal^-/H_2O$, where Mal describes malonate and uses Pitzer ion-interaction theory. This theoretical description estimates non-ideal electrostatic interactions in complex mixtures of ions in solution. The modeling activities populate Pitzer ion interaction parameters as thermodynamic descriptors of solute behavior in solution.

Summary

This year, the computational program—PitzINL—was constructed to use the compiled sets of equilibrium equations and the initially accumulated library of Pitzer parameters to model Eu^{3+} complexation by diethylenetriaminepentaacetic acid (DTPA) in a system containing an electrolyte and a buffer. The Pitzer model is used to calculate activity coefficients, and the Pitzer interaction parameters can be changed by the program user. The DTPA protonation and complexation equilibria can be calculated either with activity coefficients from the model, or using concentrations of the species present in electrolyte mixtures. The development of this computational capability illustrates the whole "building-from-the-ground-up" approach when constructing accurate thermodynamic models of solutions. The initial calculations allow tracking aqueous activities of various components in a $Eu^{3+}/H^+/Na^+/NO_3^-/H_2Mal/HMal^-/DTPA/H_2O$ system, based on Pitzer ion-interaction theory. Each time the thermodynamic model for this aqueous electrolyte mixture is refined through the addition of new Pitzer ion interaction parameters, the calculations will be revisited to observe the effects on the ion activities. This approach will indicate the importance of certain ion-ion interactions in the overall thermodynamic model. Such sensitivity analysis was performed based on theoretical calculations. The arrival of new Pitzer parameters should agree with those. When a compiled thermodynamic Pitzer model for the $Ln^{3+}/Na^+/NO_3-/H_2Mal/HMal^-/DTPA/H_2O$ system was used to reproduce aqueous electrolyte conditions present for a pH dependency study for a Talspeak-type system the trend for the activity of free europium ion matched the typically observed decreasing trend of its liquid-liquid distribution.

Benefits to DOE

This LDRD supports all four DOE energy security missions in that predictive modeling of separations would be a valuable asset to ensure the reliability of advanced nuclear fuel cycles.

Predictive modeling of solution mixtures that partake in the proposed liquid-liquid separations for the recovery of actinides from dissolved nuclear fuel has been demonstrated. The established theoretical means of prediction allow flexibility to apply similar methodology to novel mixtures if new aqueous separation processes are discovered.

Relevant Publications and Presentations

Zalupski, P.R., S.L. Clegg, L.H. Delmau, M. Nilsson, and T. Levitskaia, "Building Thermodynamic Models of Solution Mixtures to Support Predictive Modeling of Liquid-Liquid Distribution Systems," *17th Symposium on the Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 23–27, 2011.*

Zalupski, P.R., S.L. Clegg, L.H. Delmau, M. Ensor-Freiderich, M. Nilsson, M. Gray, and T. Levitskaia, "Building Thermodynamic Models of Solution Mixtures to Support Predictive Modeling of Liquid-Liquid Distribution Systems," *244th National Meeting of the American Chemical Society, Philadelphia, PA, August 19–24, 2012.*

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[1] University of East Anglia

Spatially-Correlated Microstructural Characterization: from Centimeters to Nanometers

Dawn Janney, Jill Scott, and Timothy McJunkin
10-060

INL has many scientific instruments that use spatially resolved data (i.e., data whose value can be expected to vary depending on where in the sample it was collected) on a continuum of spatial scales extending across seven orders of magnitude (from centimeters to nanometers). Because each kind of instrument looks at different characteristics of the samples, a thorough understanding of the material would require researchers to synthesize information from different instruments, collected from the same area. It is also often useful to synthesize data collected from the same area with the same instrument, even though the sample has been removed from the instrument and re-positioned.

In practice, three problems must be solved before these kinds of syntheses become possible:

- Developing techniques for finding the same area on the sample with the same instrument, after removing and re-positioning the sample

- Developing techniques for finding the same area with multiple instruments

- Allowing researchers to identify all of the data from an area, no matter what instrument it was collected with.

This LDRD addresses all these problems, creating a research tool that can be used to collect a wide variety of data (e.g., chemical, microstructural, thermal, and structural) from the same area, and to find data from each area collected using different instruments.

Summary

Key accomplishments of the project included: Designing, developing, and manufacturing a new kind of sample holder whose size and material were suitable for analysis in all of the instruments that measure spatially resolved data that we were able to identify at the INL's Materials and Fuels Complex and Idaho Research Center as well as the Center for Advanced Energy Studies (a partnership between INL and Idaho universities). The holders incorporate "fiducials" (points whose locations can be precisely measured) that can be used by each of the instruments.

The capabilities of the holders was demonstrated by loading them and measuring locations of fiducials in eight different instruments from five different commercial manufacturers, as well as one instrument designed and developed at INL. The instruments included three scanning electron microscopes, two focused ion beam instruments, a micro-focus x-ray diffractometer, an electron microprobe, and an instrument for measuring thermal properties.

Software that calculates the current instrument coordinates of points in the sample based on locations of the points in a previous measurement session and coordinates of fiducials in both sessions. The sessions may be in different instruments. The software also keeps track of which locations have been visited in each session, making it possible to find all of the data for a particular location regardless of which instrument collected it.

Another outcome included comparing calculated and experimental coordinates of specific locations in each of the instruments. Differences between these coordinates depended on the instruments involved, and typically ranged between ~2 and 60 µm. By making repeated measurements in the same instrument without moving the sample, repeated measurements in the same instrument after removing and re-positioning the sample, and cross-instrument comparisons, we were able to identify sources of error and suggest ways to remedy them. Suggested remediation techniques included improving the precision with which an instrument was aligned, developing more precise ways to measure fiducials, developing "best practice" suggestions for instrument operators, and developing custom mounting devices to reduce movement of the sample within the instrument.

Benefits to DOE

This project advances the state of the art in materials characterization. It has a wide variety of applications both inside and outside of DOE. Specific examples of interest to DOE include analysis of corrosion products formed inside existing reactors (increasing our understanding of factors that might limit the operating lifetimes of the current reactor fleet), characterizing new fuels and waste forms, and nuclear forensics (to understand and minimize risk of nuclear proliferation and terrorism). The results could also be used to benefit most other cabinet-level departments (e.g., for analyzing specific particles in soil samples analyzed for the Departments of Agriculture,

Interior, and Transportation; for characterizing materials used in prosthetic limbs for Departments of Veterans Affairs and Health and Human Services, and for obtaining detailed data used by the Department of Commerce to recognize counterfeit items).

Relevant Publications and Presentations

Janney, D.E., T.R. McJunkin, T.L. Trowbridge, and J.R. Scott, "Spatially-Correlated Microstructural Characterization: From Centimeters to Nanometers," *TMS 2011 Annual Meeting and Conference, San Diego, CA, February 27–March 3, 2011.*

Irradiation Testing and Molecular Modeling of Irradiation-Assisted Diffusion and Microstructural Evolution

Bulent Sencer, Thomas Hartmann,[1] Kenneth Czerwinski,[1] Lin Shao,[2] Yong-ho Sohn,[3] Kevin Coffey,[3] and Chaitanya Deo[4]
10-068

Irradiation of nuclear fuel in reactors results in fuel swelling and in production and transport of fission products to the cladding. The contact between fuel matrix fission products and fuel cladding will promote chemical and mechanical interactions with the cladding. The chemical compatibility between the fuel and cladding is imperative for safe operation of a reactor, and it is essential to limit the interdiffusion between the fuel and cladding. We are using ion irradiation created in an accelerator to investigate the effects different irradiation types might have on fuel-cladding interactions with prototypic material systems that have been traditionally difficult to study. Modeling efforts will be supported with this data to demonstrate the combination of testing simulated systems and modeling. The proposed study will contribute to a better understanding of fuel cladding interaction by investigating model systems coupling with the fuel materials. Fuel-cladding diffusion experiments will be conducted at temperatures of up to 600°C under proton, helium, and other heavy ion irradiation if appropriate. The various diffusion couples will be analyzed by imaging, phase analytical and chemical methods. We will use electron microscopy and other tools to investigate the interdiffusion kinetics, phase formation at the clad-fuel interface, diffusion coefficients, and the clad-fuel microstructural development.

The primary purpose of the research is to measure activation energies, both thermal and radiation enhanced. We have about ~40 diffusion couples (single and binary) for a single temperature. We will continue to prepare diffusion couples for thermal activation energies followed by irradiation to see if there is any enhancement in the interface.

Summary

This research was carried out to learn about kinetic and diffusion coefficients of the diffusion couples, which (as far as we know) has not been done before. We produce the missing data (kinetic, interdiffusion coefficients, etc.) for simple systems so that modelers can model starting from the simplest system and later move into more complex systems.

The University of Nevada, Las Vegas (UNLV), Texas A&M, the University of Central Florida (UCF), and Georgia Institute of Technology (GeTech) are the collaborators for this project. Contracts were set up with the new university partners (Texas A&M and UCF) beginning in the second year. UNLV employed one postdoctoral researcher, UCF employed one graduate student, Texas A&M employed one graduate student, and GeTech employed one graduate student.

UNLV and UCF prepared diffusion couples for characterization; they are pure Fe, Mo, Zr, Ce, Nd/alloys of Ce-50Nd, Fe-15Cr, Fe-15Cr-15Ni/diffusion couples (bonded) of Fe vs. Zr and Mo vs. Zr. These materials were irradiated with heavy ions (Fe) to 100 dpa at 450°C and 650°C. 550°C Irradiations will be carried out early in FY 2013 by Texas A&M. Characterization of 450°C and 650°C irradiation will start shortly. UNLV is working with some non-U- and U-containing diffusion couples. UNLV is ready to send the first non-U diffusion couples, and will follow with U-containing diffusion couples. UNLV samples will be irradiated by helium at three different irradiation temperatures. UNLV is helping UCF to characterize the diffusion couples with Electron Probe Micro-Analyzer. Texas A&M is also contributing to the characterization. Texas A&M used our focused ion beam to prepare transmission electron microscopy samples from different regions of several diffusion couples (Fe/Zr, Fe/Mo, that are irradiated to 100 dpa with heavy ion radiation). Several manuscripts are being prepared for journal publication on microstructure. We also calculated a number of kinetic and diffusion properties (U/Mo, U-10Zr/Fe, U/Fe, etc.). Several manuscripts are also being prepared by UCF for publication.

GeTech is using models (current and new) for verification and validation. GeTech performed a series of single point electronic structure calculations in Vienna ab initio Simulation Package (VASP) for migration barriers in bcc Mo and bcc U. The phase diagram of the Fe-U system reveals two main intermetallic phases the Fe rich Fe_2U and uranium rich FeU_6. Not much is known about these phases, so we performed first principles calculations using VASP to characterize these phases in more detail. We calculated the structural features, lattice positions, lattice parameters as well as elastic constants of these phases. GeTech is preparing a manuscript for journal publication based on this work.

Tables 1 and 2 are examples of the data produced.

TABLE 1. Results of U-Fe diffusion couple experiments showing phase thicknesses and integrated diffusion constants.

		Fe_2U Δx (μm)	σ (μm)	D^- (m^2/s)	U_6Fe Δx (μm)	σ (μm)	D^- (m^2/s)
α-U	600 C, 200 h	3.5	0.8	1.24×10^{-17}	35.4	4.3	2.31×10^{-16}
	650 C, 100 h	4.1	0.8	1.59×10^{-17}	36.8	4.5	2.50×10^{-16}
β-U	700 C, 100 h	7.1	1.4	5.22×10^{-17}	74.5	4.2	1.02×10^{-15}

TABLE 2. Lattice constants and formation energies of intermetallic structures of U-Fe. Four theoretical structures are included: B1, B2, $L1_2$ (U-rich and Fe-rich).

Phase	Strukturbericht Designation	Energy per Atom (eV)	Cohesive Energy per Atom (eV)	a_0 (Å)
UFe_2	C15	-9.387	-0.083	6.899
FeU_6	$D2_c$	-10.870	-0.0037	10.146,5.235
UFe	B1	-9.673	0.128	5.191
UFe	B2	-9.595	0.206	3.199
Fe_3U	$L1_2$	-9.116	-0.060	3.732
U_3Fe	$L1_2$	-10.080	0.467	4.194

Benefits to DOE

Interdiffusion phenomena are very important to understanding the useful lifetime of nuclear reactor components and fuels including determination of measurable materials changes associated with degradation in service that are indicative of incipient failure. One of the goals of our research activity is to determine measurable materials changes associated with degradation in service that are indicative of incipient failure. For example, fast reactor fuels are often limited in operating characteristics or lifetime by interaction of the fuel or fission products with the fuel cladding materials. Detailed models for some of these effects, such as the fuel-cladding interactions, are just now being considered and data is needed to test the models (verification and validation). It is also difficult and costly to construct in-reactor experiments to study these effects.

Relevant Publications and Presentations

None.

Nuclear Reactor Safety Case

Haihua Zhao, Ray Berry, Ling Zou, Hongbin Zhang, Samet Kadioglu, and Brandon Blackburn
10-093

Reactor system safety analysis codes play important and indispensable roles in designing advanced reactor concepts such as small modular reactors and Gen-IV reactors, supporting the licensing work for new reactor projects, implementing power updates, and licensing renewals for existing power reactors. Widely used safety codes such as RELAP5 and TRAC were originally developed more than three decades ago. Over this period, significant advances have been made in the areas of software engineering, numerical methods, and reactor thermal hydraulics and physics. Newer codes like the U.S. Nuclear Regulatory Commission's (NRC) TRACE, which combines TRAC and RELAP5, only take advantage of a small part of this progress while keeping the same numerical methods and two-phase flow physical models used in the older codes. No major effort has been made to combine all these advances together to create a foundation for new generation reactor safety analysis codes.

The original goal of this project was to quickly create a new generation production software foundation for reactor system analysis and reproduce RELAP5 capabilities. At the beginning of FY 2012, INL decided to focus resources and only develop one MOOSE-framework-based RELAP-7 code. Consequently, the project's role was changed to investigate new models and methods for improving system safety analysis capabilities. Some of this work will likely become more important in the long term.

Summary

During FY 2012, two research efforts were pursued to help address long-standing modeling deficiencies in safety analysis. The first research effort was to investigate the use and advanced a 7-equation, two-phase flow model for reactor safety simulation. It is well known that the 6-equation, two-phase flow model used for the current codes is ill posed and only becomes well posed with the help of large artificial viscosity. The grid size must be carefully selected to match experimental results. A grid size that is too small will result in divergence. Therefore, the 6-equation model cannot be used for a computational fluid dynamics (CFD)-type of verification, which requires continuous reduction of grid size so that the numerical error falls at the rate determined by the spatial discretization order. Additionally, the 6-equation model cannot capture important physics such as choked flow. To address those issues, a well-posed 7-equation, two-phase flow model was developed under previous LDRD funding. Instead of assuming equal pressure between liquid and vapor phases, two pressures are assumed and an additional void fraction equation is added to form a hyperbolic system. One of the important advantages of this model is that reduced systems are obtained naturally, characterized by instantaneous equilibrium (global or local) between mechanical equilibrium (5-equation model) and thermal equilibrium (3-equation model). This is ideal for coupling to simpler codes, "legacy" codes, or continuous reduction to simpler models (when appropriate) for faster execution speeds. This model could potentially form the theory basis of a new generation of reactor safety codes and the next generation 3-D high-resolution, two-phase CFD codes.

During FY 2012, the effort was focused on investigating the 7-equation, two phase model with a previously developed prototype code, using two types of approaches: (1) steady state compressible flow through nozzles covering critical flow, flow discontinuities, and transitions to supersonic flow, by using Deich nozzle and Moby-Dick nozzle tests; and (2) rapid depressurization of pressure vessels and pipes (blowdowns) to cover shocks, rarefactions, contact surfaces by using Edwards pipe and Cannon experiments. These experiments were widely used for validation for the last generation of codes.

The second research effort was to develop new methods to describe flow junction/branch models for both incompressible and compressible flow in order to remove any inconsistency in the models currently used in RELAP5, TRAC, or TRACE. Reactor systems are complex pipe networks composed of many 1-D pipes connected by valves, fittings, and plenums. Inside those flow junctions, fluid flow is 3-D. However, to be practical for reactor system analysis, 0-D models with the help of empirical correlations must be used to approximate the complex physics. The flow junction models currently used in system codes are based on an incompressible flow assumption and are problematic for compressible flows. Significant effort was spent investigating the non-trivial, correct, and robust flow junction physics to treat compressible flows. Three different methods were examined: (1) classical thermodynamics approach that was used by existing codes, except—in this instance—the thermodynamics process must be known or assumed;

(2) a general continuum mechanics approach which is newly proposed; and (3) a method of characteristic approach which is also new.

Besides these two focus areas, additional preliminary work was performed primarily by two summer graduate student interns. One used forward sensitivity analysis method to quantify numerical errors in 1-D flow equations. The forward sensitivity method is an intrusive method for sensitivity and uncertainty quantification. Time and space discretization sensitivity analysis can be used to minimize numerical errors and find proper time and space steps. Overly refined time and space discretization wastes computational time and overly coarse time and space discretization results in numerical errors dominating physical uncertainties. Figure 1 shows one sample

problem where the left figure is a momentum wave solution and the right figure is the corresponding time-step sensitivity. The time integration error on momentum can be estimated by the multiplication of the time-step sensitivity for momentum and the time step.

Benefits to DOE

This project will enable critical tools and methods for creating science-based advanced nuclear reactor safety codes that will benefit both regulating agencies and the nuclear energy industry. Increasing the percentage of energy from nuclear power reduces the amount of greenhouse gas emissions. Nuclear power reduces our nation's dependence on foreign energy sources, which increases our national security.
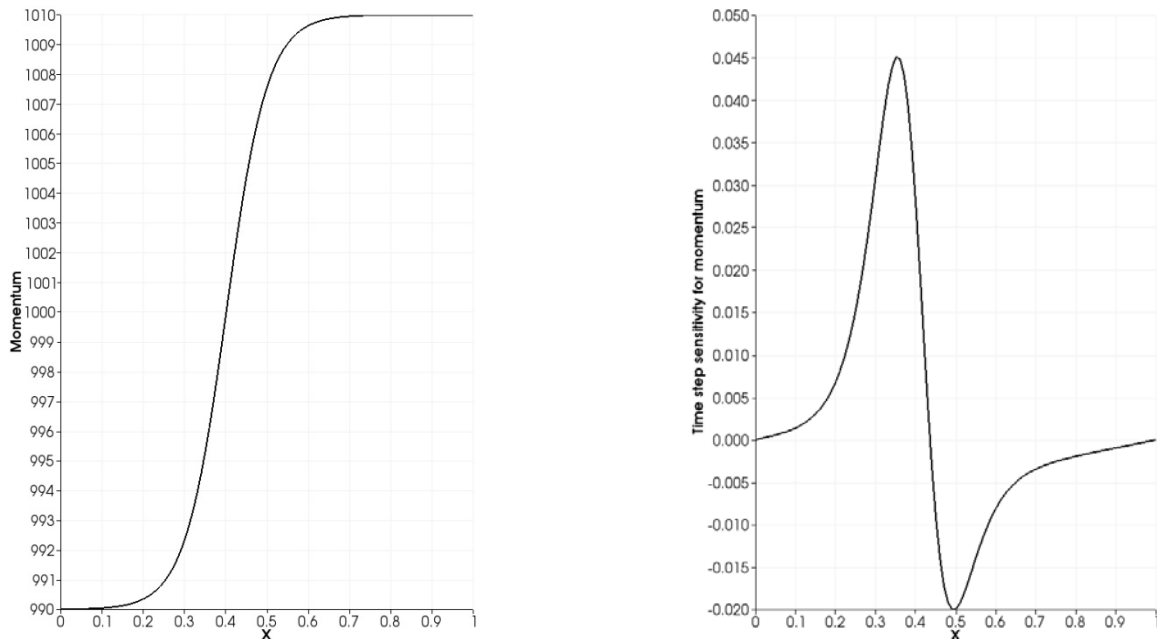
FIGURE 1. Isothermal 1-D flow momentum solution (left) and time-step sensitivity for momentum (right) at t = 0.01 with $\Delta t = 0.001$, $\Delta x = 0.005$.

Relevant Publications and Presentations

Wang, X., X. Sun, B. Doup, and H. Zhao, "Dynamic Modeling Strategy for Flow Regime Transition in Gas-Liquid Two-Phase Flows," *Journal of Computational Multiphase Flows,* Vol. 4, 4, 2012.

Zhao, H. and V.A. Mousseau, "Extended Forward Sensitivity Analysis for Uncertainty Quantification," *Nuclear Technology*, Vol. 181, 1, 2013.

Zhao, H. and V.A. Mousseau, "Use of Forward Sensitivity Analysis Method to Improve Code Scaling, Applicability, and Uncertainty (CSAU) Methodology," *Nuclear Engineering and Design*, Vol. 249, 188–196, October 2011.

Zhao, H., H. Zhang, and L. Zou, "An Efficient Modeling Method for Thermal Stratification Simulation in a BWR Suppression Pool," *The 9th International Topical Meeting on Nuclear Thermal-Hydraulics, Operation and Safety (NUTHOS-9), Kaohsiung, Taiwan, September 9–13, 2012.*

Zhao, H., H. Zhang, L. Zou, and X. Sun, "Enhancing VHTR Passive Safety and Economy with Thermal Radiation Based Direct Reactor Auxiliary Cooling System," *Proceedings of ICAPP '12, Chicago, USA, June 24–28, 2012.*

Haptic Tele-Operated End Effector for Hazardous Environments

Anthony Crawford and Jeff Molitor
11-000

Natural movements and force feedback are important elements in using remote-handled equipment to quickly perform complex manipulation tasks in hazardous environments such as hot cells, glove boxes, decommissioning, explosives disarmament situations, and space exploration. We are developing a system to provide users with the ability to fully utilize their natural dexterity and the force sensations in their hands to enhance remote-handling performance. To that end, our objective is to enhance the user's ability to perform tasks in hazardous environments via a radiation-hardened robotic end effector with the form and function of a human hand/arm and an adaptable haptic (force feedback) user interface.

If successful, this technology will increase the rate of performing in-cell tasks with the state-of-the-art manipulators by a factor of five to ten. This work revolutionizes the current remote manipulation technologies that are predominately based on a design patented in 1945. Novel contributions of this work include the application of haptics to potentially radioactive environments, the design of a flexible/transparent haptic user interface mechanism (most current haptic systems use cumbersome gloves), investigating optimal techniques to scale a user interface's force workspace with that of its corresponding robotic counterpart, and algorithms to identify the geometric properties of the user's hand and automatically adjust the hand controller to accommodate. The system also has benefits in nonhazardous environments including virtual reality, medical rehabilitation, expertise training, and a more thorough understanding of how humans physically interact with the world and machines.

Summary

Since it began in FY 2011, this LDRD project has made significant progress in the development of a haptic hand user interface, a corresponding robotic hand, and the associated haptic controller hardware/algorithms. The haptic hand user interface has been designed, prototyped, and tested. The user interface has been shown to have sufficient flexibility (Degrees of Freedom [DOF] and range of motion) to allow the user to move their fingers throughout their full range of motion. The user interface has also exhibited sufficient speed such that it is able to move in unison with a user's rapid movements without inhibiting the said movements (this process is known as

transparency). Such a condition arises when the corresponding virtual or robotic fingers are rapidly approaching an object but have yet to make contact. The device also has sufficient strength to communicate the necessary levels of force such that the user can appropriately interpret the environment and use that information to execute the intended task, whether that task is manipulation or grasping. Other hand user interfaces are limited to either manipulation or grasping activities, but not both. This is generally because the stronger devices have less flexibility due to a reduced number of DOF and are generally limited to just grasping tasks while the devices with more flexibility are generally weaker and limited to just light manipulation tasks.

In addition to the user interface's unique mechanical form, we have also developed a unique nonlinear strength profile relating the force experienced by the virtual environment or robotic hand to the user interface. The employed nonlinear profile demonstrates enhanced performance when executing various tasks because— unlike the traditional linear profile—the nonlinear profile compliments the differences between manipulation and grasping tasks including task complexity, task frequency, number of dominant muscles, user fatigue, the human's ability to sense just noticeable force differences, and the associated brain activity. As a result, the physical capabilities of the device are optimized based on the physiological properties of the human hand and mind.

The nonlinear profile is employed in the algorithms embedded in LabVIEW and run on a real-time Field-programmable gate array controller that provides the appropriate feedback frequency (1 kHz) in order to achieve effective haptic control. The hardware necessary to communicate with the motors and sensors has also been developed for the haptic user interface to operate its DC motors and is under construction to operate the brushless DC motors and resolver position/velocity sensors being embedded in the robotic hand.

The brushless DC motors and resolvers are being employed in the robotic hand because they are known radiation tolerant technologies. The robotic hand has been designed to be anthropomorphically accurate and has 20 of the human hand's 22 DOF such that it can appropriately reflect the user's movements. The robotic hand also has compliant features at its finger tips, providing the device with the ability to more readily

accommodate objects of various shapes and sizes as well as handle potential impulses that would damage traditional stiff grippers.

Benefits to DOE

The product of the research increases the quality and speed of conducting energy, nuclear, environmental, and science experiments that require remote handling in a hazardous environment. The increased speed also reduces the time that contents of an experiment are exposed to theft or unapproved examination.

Relevant Publications and Presentations

Crawford, A.L., "Force Control and Nonlinear Master-Slave Force Profile to Manage an Admittance Type Multi-Fingered Haptic User Interface," *Proceedings of ISRCS 2012, Salt Lake City, UT, August 2012.*

Crawford, A.L., "Nonlinear Force Profile Used to Increase the Performance of a Haptic User Interface for Teleoperating a Robotic Hand," *Proceedings of NPIC & HMIT*, *San Diego, CA, 2012.*

Speciation Behavior of Americium Oxidation States for the Separation of Americium from Curium in Nuclear Processing

Catherine Riddle, Patricia Paviet-Hartmann, and Ken Czerwinski[1]
11-005

Many countries are currently expanding nuclear energy as a method for the safe generation of carbon-free energy. Closed fuel cycle technologies are key to waste reduction and a sustainable nuclear energy future. In order to support closing the nuclear fuel cycle, advanced separation technologies are being developed to effectively perform the difficult separation of the actinides, including americium (Am), from the lanthanides as well as the separation of Am from curium (Cm). This will allow the actinides to be recycled to reactors, reducing the long-term heat load and radiotoxicity of the waste requiring geological disposal. Researchers are investigating novel separation schemes that use the higher oxidation states of Am in order to separate it from the lanthanides and Cm in used nuclear fuel reprocessing. Higher Am oxidation states have long been known to exist but are less well studied and an investigation of the behavior of Am oxidation states would be an important step toward solving this difficult separation issue.

In this project, we are examining the stereochemical arrangements of atoms in close proximity to Am in different oxidation states using X-ray absorption fine structure spectroscopy (XAFS) analysis and single crystal x-ray diffraction (XRD). XAFS analysis is being used to develop an atomic picture of Am higher oxidation states in aqueous solution—which has not been previously performed to our knowledge—to better understand the processes taking place. Single crystals of Am(+V) and Am(+VI) have not been previously produced using bismuthate. The synthesis of this actinide crystal as well as subsequent analysis will play an important role in the characterization of oxidized Am species. The data from both XAFS and the crystallography work will be developed using Density Functional Theory (DFT) as a computational characterization method adding further information on the behavior of oxidized Am. Ultimately this work will result in a data-based model to be used in the separation of species with very similar chemical properties.

Summary

The second year objectives for this project included preparation of Am samples for analysis by XAFS, baseline characterization of Am(+III, +V, and +VI) oxidation states using XAFS with adjustment for noise reduction, analysis of ground state Am and oxidized Am by DFT, and continued progress toward completion of the PI's doctorate in radiochemistry. Initial baseline research on oxidized Am using XAFS was accomplished at Argonne National Laboratory's (ANL) Advanced Photon Source (APS). This data showed a distinct increase in energy, proving that characterization of Am(+V, +VI) oxidation states with XAFS is possible. Refined experiments, which are the result of what was learned from the baseline experiment, were designed to enhance the Am signal and minimize the background noise within the XAFS spectra. Beam time was procured from the Stanford Synchrotron Radiation Light Source (SSRL) for the XAFS analysis and the samples were prepared in our collaborator's facility at the University of Nevada, Las Vegas (UNLV) under the direction of the PI. A key research development resulting from the UNLV analyses is the spectra of the Am/bismuthate solutions prior to the samples being sent to SSRL. The data showed no oxidation of Am in the samples and the experiment using XAFS was put on hold until the problem could be identified and resolved. The redox problem, identified late in FY 2012, was due to peroxides (a common reducing agent) in the sodium bismuthate stock chemical. Peroxide is used in the production of sodium bismuthate and remains unevenly dispersed at approximately 20% by volume. These pockets of peroxide have the effect of randomly reducing the Am so the results show either complete oxidation, partial oxidation, or no oxidation of Am in any given experiment. This problem has been remedied by using a new purified sodium bismuthate in which the peroxides have been completely removed. Using the new peroxide free bismuthate, the oxidation shows consistency in Am oxidation data and will allow the XAFS experiment to go forward in FY 2013 at ANL using the APS beam line. Beam time for XAFS will be secured at APS by our UNLV collaborator as well as potential beam time at Los Alamos National Laboratory (LANL) through a newly established collaborative effort. The XAFS data will give definitive oxidation state information which will be analyzed through DFT.

A key development in the project this fiscal year was the experimental design and subsequent synthesis of $NaBa_3BiO_6$ Mn crystals in which the Bi(V) oxidation state was retained allowing the Mn^{+4} to be oxidized to Mn^{+7}. This crystal is a precursor to developing oxidized Am(V) and Am(VI) crystals through thermal fusion methods. The thermal crystal synthesis of these oxidized manganese

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crystals shows it will be possible to oxidize Am. The synthesis of oxidized Am(+V) and Am(+VI) crystals will be accomplished in FY 2013 with the assistance of both LANL and UNLV collaborators. In FY 2012, baseline crystal synthesis of several types of crystals, all of which retain the Bi(V) oxidant, have yielded one specific crystal compound as an excellent candidate for use in the Am experiment. The research accomplished in the past two fiscal years has advanced the PI's Ph.D. dissertation research as well as advancement to doctoral candidacy which was achieved in May 2012. Graduation from the Radiochemistry Ph.D. program at UNLV is projected for the end of FY 2013. Overall, the LDRD research is proceeding as planned and thus far includes: establishment of a successful collaboration with UNLV and potentially LANL, knowledge in XAFS measurements of actinides, crystal synthesis/analysis of actinides, and DFT analysis.

The involvement of university partnering with INL will open more avenues for targeted funding agencies and enhance the training of the future workforce. The collaboration with other national laboratories, such as LANL, will foster new funding avenues as well as promote future areas of research. This project's research is the basis for the PI's dissertation in partial fulfillment of a Ph.D. in radiochemistry from UNLV and will ultimately benefit both INL and DOE by producing a new Ph.D. in radiochemistry.

Benefits to DOE

Separation of Am from lanthanides and Cm is a key focus of DOE-NE. This research will lead to a better understanding of the behavior of this actinide species in both complexed and uncomplexed forms in the stages prior to, during and post separation as well as the separation of trivalent actinides from the lanthanides.

Relevant Publications and Presentations

Riddle, C., P. Paviet-Hartmann, K. Czerwinski, F. Poineau, P. Weck, and T. Hartmann, "Speciation Behavior of Americium Higher Oxidation States for the Separation of Americium from Curium," *American Chemical Society 242nd National Meeting & Exposition; Division of Nuclear Chemistry and Technology for the session: Celebration of the 100th Anniversary of Madame Curie's Nobel Prize in Chemistry, Denver, CO, August 28– September 1, 2011.*

Riddle, C., P. Paviet-Hartmann, K. Czerwinski, F. Poineau, P. Weck, and T. Hartmann, "Speciation Behavior of Americium Higher Oxidation States for the Separation of Americium from Curium," *Separation Science and Technology Conference, Gatlinburg, TN, October 23–29, 2011*.

Riddle, C., P. Paviet-Hartmann, K. Czerwinski, F. Poineau, P. Weck, and T. Hartmann, "Americium (V, VI) Speciation in Acidic Solution Using XAFS." (in preparation)

Riddle, C., P. Paviet-Hartmann, K. Czerwinski, F. Poineau, P. Weck, and T. Hartmann, "Bismuthate Oxidized Manganese Single Crystal Compound for Improved Alkaline Battery Energy Storage." (in preparation)

Riddle, C., P. Paviet-Hartmann, K. Czerwinski, F. Poineau, P. Weck, and T. Hartmann, "A Crystalline Bismuthate Complex of Pentavalent and Hexavalent Americium." (in preparation)

Development of a Simplified Soft Donor Technique for Trivalent Lanthanide Actinide Separations

Leigh Martin, Louise Natrajan,[1] and Clint Sharrad[1]
11-023

We are attempting to understand the various chemical processes that may lead to the successful separation of the trivalent lanthanides from the trivalent actinides. In particular, this project is exploring a novel extraction system that uses an amino acid buffer and/or short chain peptides to complete this difficult separation in a more simplistic manner compared to existing methodologies. The work being performed is not only addressing lanthanide and actinide coordination chemistry with these ligands but the effects of radiolysis on the separations.

Summary

The research performed in FY 2012 expanded on the results of FY 2011 through increasing the number of amino acids under study for separations performance and investigating the radiolytic stability of the L-alanine based separations system. The new amino acids used to buffer the aqueous phase include L-arginine, L-methionine and L-histidine. These amino acids all contain larger and more hydrophobic side chains compared to L-alanine and lactic acid. As a result, these new amino acid buffers under study were more insoluble. Despite these insolubility issues, extraction studies were completed using 0.5 M amino acid buffer at pH 2. The distribution ratios for Am^{3+} in the L-arginine and L-histidine systems were similar to the L-alanine system, however, for the L-methionine systems, the D_{Am} was 0.17, reduced by a factor of 2.5 compared to the L-alanine system. Overall, the separation factors for La^{3+}, Ce^{3+}, Nd^{3+}, and Eu^{3+} with Am^{3+} appear to be slightly elevated when the amino acid buffer side chains contain soft donor nitrogen and sulfur atoms, with the exception of Ce^{3+} in the L-arginine system. The distribution ratios for Am^{3+} and separation factors

for some lighter lanthanides from L-arginine, L-histidine, and L-methionine buffered TALSPEAK are shown in Table 1. We have started to model the solvent extraction data using an existing model. The model fits the experimental results reasonably well up to pH 3.25, despite limited availability of the necessary thermodynamic constants required for the model.

Two approaches have been used to study radiolysis effects on the L-alanine based separation system, pulsed radiolysis and γ-radiolysis. Pulsed radiolysis was used to study the $^{\bullet}OH$ radical reaction kinetics with L-alanine as a function of pH and temperature. Traditional solvent extraction experiments using γ-irradiated solvents were performed to study the effects of radiolysis on the actinide/lanthanide separation factors. In traditional TALSPEAK, it has been identified that lactic acid/lactate ion protect the DTPA ligand (diethylenetriamine-N,N,N',N'',N''-pentaacidic acid) responsible for the separation. These experiments showed that the $^{\bullet}OH$ radical reacts more slowly with L-alanine than with lactic acid (room temperature rate constant $\sim 8.32 \times 10^7$). Indeed, when these experiments were performed as a function of temperature, we learned that the activation energy for the reaction (E_a) was 12.2 kJ mol^{-1}. This is lower than that reported for the lactate ion. These results were expected to negatively affect the separation performance of the L-alanine based TALSPEAK. A slower reaction of L-alanine with $^{\bullet}OH$ radical was expected to yield more interaction with DTPA. The γ-radiolysis solvent extraction experiments were performed as a function of pH (2–3), dose (0–100 kGy) and buffer concentration

TABLE 1. Distribution ratios for Am^{3+} and a comparison of separation factors for lighter lanthanides from the L-arginine, L-histidine, and L-methionine buffered TALSPEAK extraction system at pH 2.

Buffer	Concentration (M)	pH	D_{ratio} Am^{3+}	Separation Factors			
				La/Am	Ce/Am	Nd/Am	Eu/Am
Arginine	0.5	2	0.27 ($\pm$0.01)	184	40	27	72
Histidine	0.5	2	0.40 ($\pm$0.01)	208	95	24	83
Methionine	0.5	2	0.17 ($\pm$0.01)	271	97	26	60

[1] University of Manchester, United Kingdom

(0.5–1.5 M). In all cases there was little observable effect on the separation factors as all of these variables were changed (Figure 1 and Table 2). These results are encouraging as this separations system can be considered as radiolysis resistant.
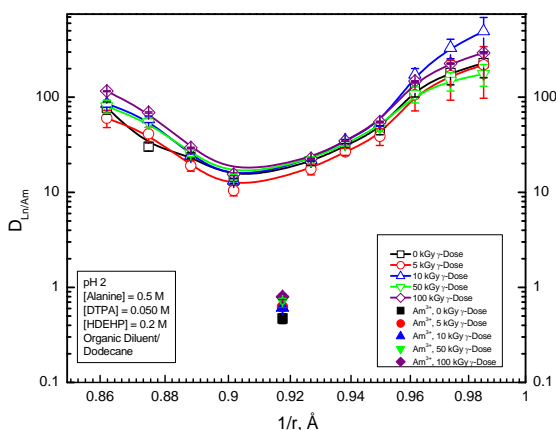
FIGURE 1. Effect of increasing γ-dose on Am^{3+}/Ln^{3+} separation.

TABLE 2. Separation factors for Eu^{3+}/Am^{3+} separation in the presence of L-alanine at 0.5 M when subjected to different doses of γ-radiation.

	S.F. Eu/Am			
pH	5 kGy	10 kGy	50 kGy	100 kGy
2	56.2	55.19	51.32	51.03
3	15.9	16.53	15.89	12.52

At the University of Manchester, a range of amino acids have been shown to bind with an Ln^{3+}-DTPA complex by luminescence spectroscopy. Emission and excitation data for the *f-f* and aromatic bands suggests there is fast exchange between bound and unbound amino acid, showing a significant interaction between DTPA and the amino acid in the extraction process. This work will be expanded at INL in the forthcoming year with Cm^{3+} using a newly procured fluorimeter. In addition to this work, experiments are underway to understand the complex formation in the organic phase medium (0.2 M Di-(2-ethylhexyl) n-dodecane) using spectrophotometric techniques and Nuclear Magnetic Resonance. X-ray absorption spectroscopy has also been carried out on a number of $[Ln(DTPA).xH_2O]^{2-}$ complexes in different environments in order to determine the effect of changing the chemical environment on the coordination of the complexes. This work is in progress and is expected to be completed in FY 2013. In addition to these activities, we have hosted a Ph.D. student from the University of Manchester at INL to teach solvent extraction chemistry and instructed the student in the proper use of macro americium work, which is not possible at the University of Manchester. This was a successful activity and it is expected that this student will return to INL again in FY 2013.

Benefits to DOE

This research is providing otherwise unavailable data on the long term performance of viable actinide/lanthanide separations processes. Further, it is contributing to the design of an advanced fuel cycle that is resistant to nuclear proliferation. All of these efforts relate to DOE's nuclear energy goals.

Relevant Publications and Presentations

"Lanthanide Actinide Separation Using an Aqueous-Modified TALSPEAK Process: Amino Acid Buffers," *Industrial and Engineering Research Chemistry,* 2013. (in preparation)

"Alanine Radiolysis and its Effects on Lanthanide Actinide Separations," *Industrial and Engineering Research Chemistry,* 2013. (in preparation)

Martin, L.R., C. Sharrad, L. Natrajan, R.D. Tillotson, P.R. Zalupski, and T.S. Grimes, "Development of a Simplified Soft Donor Approach to Trivalent Actinide/Lanthanide Separations," *17th Symposium on Separations and Technology for Energy Applications, Gatlinburg, TN, October 23-27, 2011.*

Martin, L.R., R.D. Tillotson, and T.S. Grimes, "Radiation Effects on An^{3+}/Ln^{3+} Separation in Amino Acid Buffered TALSPEAK," *Actinide Separations Conference, Chattanooga, TN, May 21-24, 2012.*

Grimes, T.S., R.D. Tillotson, and L.R. Martin, "Lanthanide/Actinide Separation Using Aqueous-Modified TALSPEAK Chemistry," *Actinide Separations Conference, Chattanooga, TN, May 21-24, 2012.*

Grimes, T.S., R.D. Tillotson, and L.R. Martin, "Radiolytic Stability of a Modified TALSPEAK Process," *67th Northwest Regional Meeting of the American Chemical Society, Boise, ID, June 24-27, 2012.*

Langford, M., C. Sharrad, L. Natrajan, T.S. Grimes, and L.R. Martin, "Development of a Simplified Soft Donor Approach to Trivalent Actinide/Lanthanide Separations," *ATALANTE 2012, Montpellier, France, September 2–7, 2012.* (invited*)*

Development of In-Reactor Experiment Configuration for Laser-Based Material Properties Measurement

Robert Schley, Dave Hurley, and Rory Kennedy

11-037

The measurement methodology put forth by this project will advance the state of the art for in-reactor measurements and provide significant benefit to ATR users by enabling real time monitoring of material property evolution. This work addressed the need for in-reactor measurement of mechanical properties during irradiation. The objective was to develop and demonstrate a prototype test capsule incorporating optical-fiber-based measurement of mechanical properties in an experimental configuration suitable for use in the ATR.

Summary

Project work began with the intent of using surface acoustic wave velocity as a method of detecting changes in material properties. As detection of the surface acoustic waves in the intended environment proved elusive, a test configuration for measuring the natural frequency of small cantilever beams was developed. The test configuration was demonstrated by monitoring the elastic property change of a copper sample as it underwent recrystalization at elevated temperature.

The redistribution of porosity in ceramic nuclear fuels during irradiation is of great interest to the fuel development community. During the initial surface acoustic wave investigations, a commercial optical-fiber-based interferometer was used to measure surface acoustic waves on a cerium oxide sample. A reflective foil on the surface of the cerium oxide was required to collect sufficient light for detection. Although the surface acoustic waves were discernable in the resulting signal, without the reflective foil, detection of these waves in a reactor environment was deemed unlikely. Therefore, we sought the measurement of phenomena more likely to be successful in the reactor environment.

The natural frequency of a vibrating beam is a function of its density, dimensions, and modulus of elasticity. Consequently, measuring changes in the natural frequency of vibration can be used to monitor changes in the elastic properties of the beam material. Based on this concept, an experiment configuration that incorporated optical fiber excitation and detection was developed to monitor the flexural vibrations of a thin cantilever beam. The cantilever beam was machined into a square frame that could be clamped between the top and bottom plates of a test capsule. The test capsule allowed for precise placement of the beam and alignment of fiber optic probes. Figure 1 shows a composite photo of a copper cantilever beam sample on the left and the assembled test capsule with the optical fiber probes on the right. Detection was based on a fiber optic lever technique in which light emanating from a fiber tip is reflected from the target and coupled back into the fiber. The intensity of the return light is a function of the fiber tip to target distance so that the vibrating beam modulates the return light intensity. This detection technique has the advantage of not requiring additional optics or complicated alignments—simplifying its use in a reactor test capsule. Beam excitation was provided by a chopped laser source delivered to the base of the beam. A network analyzer was used to sweep the chop frequency of the excitation source while recording the signal from the detector.
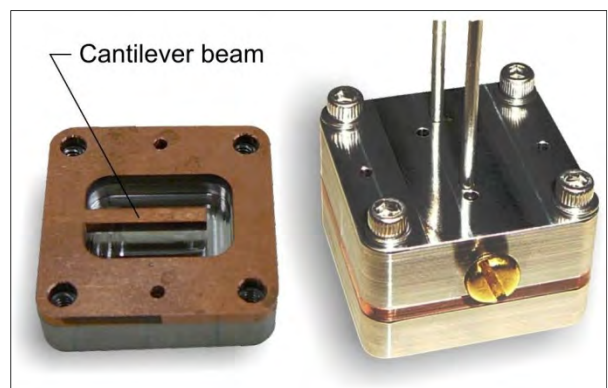
FIGURE 1. Copper beam plate (left); assembled test capsule with excitation and detection optical fibers probes (right).

The experimental technique and its applicability to in-reactor measurements were demonstrated by monitoring the elastic modulus changes of a sample as it was annealed in a tube furnace. The sample was fabricated from high purity copper that had been rolled to produce a highly deformed grain structure. Upon annealing, the copper recrystalizes creating new undeformed grains and a permanent reduction in the elastic stiffness. The results of the test are shown in Figure 2, which is a plot of the resonant frequency of the copper cantilever beam vs. the furnace temperature. As shown, the initial resonant frequency was 1,135 Hz corresponding to an elastic modulus of 118 GPa. Recrystalization began at approximately 150°C with a corresponding drop in the beam frequency. After cooling a resonant frequency of 878 Hz was measured corresponding to an elastic modulus of 70 GPa. These results demonstrate the ability to measure mechanical properties changes using the in-reactor compatible configuration developed in this project.
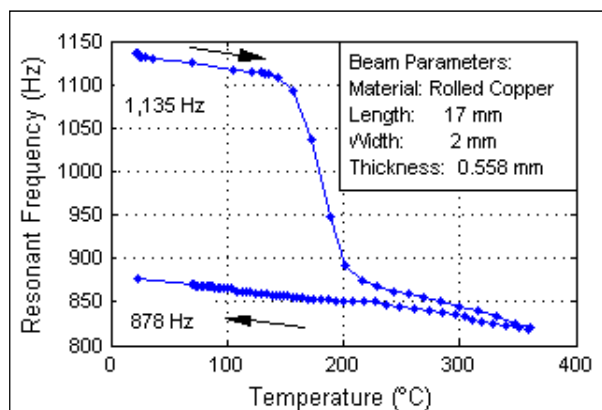
FIGURE 2.Top: Laser pulse induced beam oscillations. Bottom: Beam resonant peak induced by chopped laser.

Benefits to DOE

New in-reactor measurement capabilities will support DOE-NE's Advanced Nuclear Energy Initiative. The methodology and experimental configuration developed in this project could be used for in-reactor measurements of material properties. This capability will provide a powerful new tool for ATR NSUF users to assess radiation effects on materials in real time.

Relevant Publications and Presentations

Farzbod, F., R.S. Schley, and D.H. Hurley, "Resonant Ultrasound for a Cantilever Sample," *Journal of Applied Physics*. (submission planned)

Schley, R.S., Z. Hua, D.H. Hurley, and H. Ban, "Optical Fiber Technique for In-Reactor Mechanical Properties Measurement," *presented at the Review of Progress in Quantitative NDE, Denver, CO, July 2012.*

Schley, R.S., Z. Hua, and D.H. Hurley, "Optical Fiber Technique for In-Reactor Mechanical Properties Measurement," *(in press) proceedings Review of Progress in QNDE, 2012.*

Alternative Processing for Improved UO$_2$-Based Fuels

Paul Lessing, Pavel Medvedev, and Roger Cannon[1]

11-051

This project is studying improved processing/fabrication for nuclear fuels. Specifically, the basic studies to improve processing/fabrication technologies to improve in-reactor performance of nuclear fuel pellets include: the role of moisture content as a lubricant and binder in pressing pellets, factors affecting the selection and performance of polymeric binders and lubricants, the effect of fuel-generated radiation upon binder performance, ways in which dry bag isostatic-pressing can replace metal-die pressing to produce more homogeneous and stronger pellets, development of a "dry" process (for use in inert gloveboxes) to create rounded granules that flow freely and homogeneously when filling pressing bags and dies, and the elimination of traditional time-consuming steps (e.g., "slugging" to produce high density granules) that are expensive and produce non-round granules.

Summary

Currently we are using CeO$_2$ as a surrogate ceramic, but depleted UO$_2$ can be studied. We developed a crack model to predict the toughness of green ceramics based upon the binding forces of meniscuses formed between particles near the tip of a critical flaw (Figures 1 and 2). The calculated fracture toughness values were in approximate agreement with those of green ceramics we fabricated with no binders but having two different specific surface areas. We finished the investigation of loss of green pellet strength due to radiation damage to their organic binders from the Am and Np content of transuranic-mixed oxide (TRU-MOX) pellets. The results were written as a journal submission, peer reviewed, and the paper is ready for submittal. Fracture strength degraded continuously over the 10 days of the study for three representative binders. Of these binders, only a Styrene-acrylic copolymer retained sufficient strength after one week to allow a pellet to continue on to the high temperature sintering process (Figure 3). A third paper is being written that characterizes the details of the radiation-induced degradation mechanisms of films made from the organic binders. Figure 4 represents the extent of radiation damage. Our focus moved away from radiation damage to binders that aid in the spheronization of granules, dry-bag isostatic pressing, and machining of fuel pellets. This "dry" processing can be applied to the fabrication of a variety of improved and accident-resistant

Light Water Reactor fuel pellets. We are well on the way to developing a process that leads to better performing, homogeneous pellets that can be fabricated to a "near-net shape" with very minimal distortion of dimensions during the firing process. Figure 5 shows a segment of iso-pressed rod that was subsequently fired/sintered to its final high density.
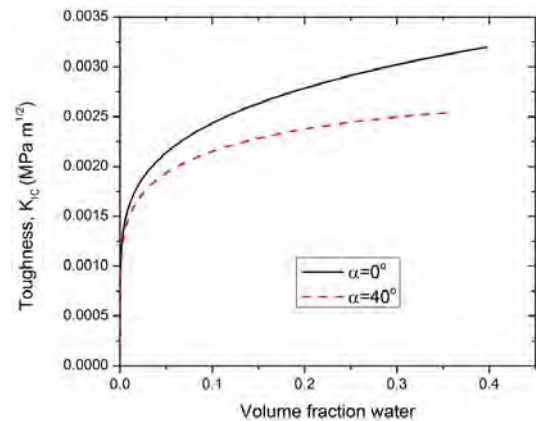
FIGURE 1. Toughness vs. vol. fraction H$_2$O for a non-agglomerated powder.
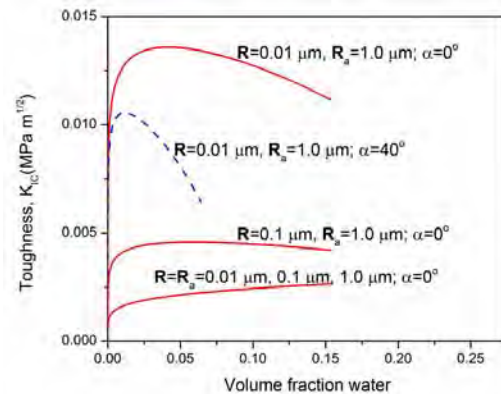
FIGURE 2. Toughness vs. vol. fraction H$_2$O for an agglomerated powder.

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[1] Rutgers University, Emeritus
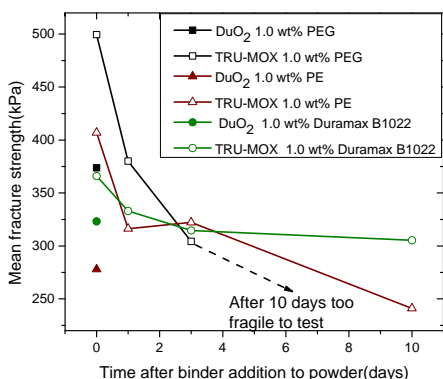
FIGURE 3. Loss in fracture strength of TRU-MOX pellets with time due to radiation damage to various organic binders.

(a)

(b)

(c)
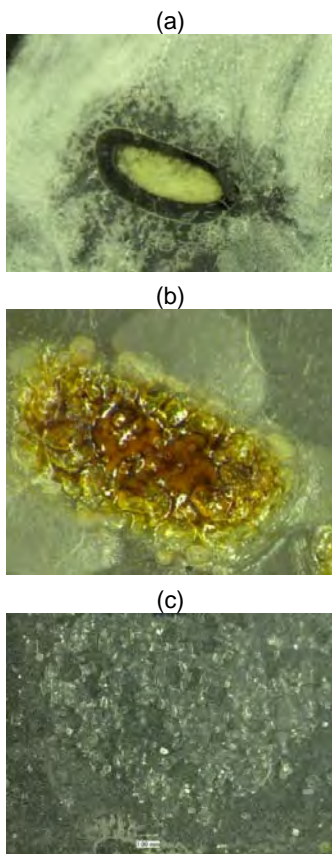
FIGURE 4. Accelerator (alpha) irradiated (1×10^{14} fluence, Li^+ 30 MEV) binder films: (a) Polyethyelene Glycol (Carbowax), vaporization and severe damage, (b) Polyethylene (Crystalcer X), bubbling from decomposition gases, (c) Styrene-Acrylic (Duramax B1022), cracking.

FIGURE 5. Portion of sintered CeO_2 rod originated from a Dry-Bag Isostatic Pressed, long "green" rod.

Benefits to DOE

Variations on our new fabrication techniques will prove to be innovative and valuable to ceramic fuel pellets for industrial Light Water Reactors, including MOX and Inert Matrix Fuel benefitting DOE-NE. The results can be directly applied to the enhanced fabrication of UO_2-based fuels of interest to DOE-NE such as MOX ($UO_2 + PuO_2$), TRU-MOX from recycled fuel ($UO_2 + PuO_2 +$ actinides) and enriched UO_2. The project builds INL equipment capability in fabricating UO_2 and other powder-processing based fuels, and the knowledge can be applied to other fuel compositions such as carbides, nitrides, and intermetallics for potential use in accident tolerant fuel systems.

Relevant Publications and Presentations

Lessing, P.A., "Alternative Processing of Improved UO_2-Based Fuels," INL external peer review committee, Idaho Falls, ID, June 23, 2011.

Cannon, W.R., P.A. Lessing, and L.D. Zuck, "Crack Model for Toughness of Green Parts with Moisture or a Fluid Binder," *Am. Ceram. Soc.,* Vol. 9, 2957–2964, 2012.

Lessing, P.A., W.R. Cannon, G.W. Egeland, L.D. Zuck, J.K. Jewell, D.W. Akers, and G.S. Groenewold, "Strength Loss in MA-MOX Green Pellets from Radiation Damage to Binders," completed, to be submitted to the *J. of Nuclear Materials.*

Groenewold, G.S., W.R. Cannon, P.A. Lessing, R. Avci, M. Deliorman, M. Wolfeden, J.K. Jewell, D.W. Akers, and L.D. Zuck, "Characterization of Polymeric Films Subjected to Lithium Ion Beam Irradiation," DRAFT, 2012.

31

Spatially Resolved Positron Analysis of Hydride Formation in LWR Fuels with GE-Global Nuclear Fuels

Douglas Akers, Mark Drigert, Maria Okuniewski, Paul Cantonwine,[1] and Tony Hill[2]
11-055

Hydride formation in commercial nuclear fuel zircaloy cladding is one of the critical issues limiting the lifetime of commercial nuclear fuel designs to about 80 MWd/kgU. General Electric-Global Nuclear Fuels (GE-GNF) has developed a CRADA with INL to develop INL's Spatially Resolved Positron Annihilation (SRPA) technology to provide in situ, nondestructive measurements of hydride formation in nuclear fuel cladding and components following irradiation. The SRPA is a novel technology that has received an INL patent. This technology provides an improved fundamental understanding of the atomic-level microstructure of GE-GNF reactor fuel cladding and the effects of hydride formation on the lifetime of the cladding when exposed to long-term irradiation. In addition to developing an understanding of hydride damage effects it provides a basis extending current reactor fuel lifetimes, minimizing waste and developing new reactor fuels.

Verification and testing of the SRPA method for characterization of nuclear fuel cladding for hydride production is being performed using surrogate samples containing hydrogen at INL, development of a strain measurement capability to assess strain effects in cladding, and irradiated cladding measurements at the GE Vallecitos facility. The project includes a strong cross correlation component that will connect the SRPA data, ex-situ measurement data currently used for hydride characterization, and the effects of strain and irradiation damage on the cladding. These data will be used to develop the design of a pool side SRPA system that can be used by GE-GNF to perform in situ characterization of fuel cladding for hydride content at GE fuel storage facilities. In addition to the direct application of the SRPA technology to the GE-GNF's current and advanced Light Water Reactor (LWR) fuels programs, the SRPA technology has specific applications to other nuclear fuel-related issues such as fuel cladding interaction and stress corrosion cracking.

Summary

Progress during the first year of this project includes: (1) an extensive series of SRPA measurements on a range of samples containing hydrogen, (2) cross correlation of the SRPA data with ex-situ measurement techniques such as optical metallography and Scanning Electron Microscopy (SEM), (3) development and testing of an SRPA based strain measurement system that allows direct measurement of strain phenomena in the cladding at levels as low as 0.05% strain, (4) development and testing of an SRPA scanning system suitable for use in high radiation fields and on irradiated zircaloy specimens, and (5) the development of initial conceptual designs for both hot cell and poolside basin scanning systems for use at GE-GNF facilities. GE-GNF technical experts have been involved in these efforts and have begun planning for implementation of the irradiated zircaloy cladding measurement system at the GE-GNF Vallecitos facility and for implementation of SRPA measurement systems for testing at the GE-GNF Wilmington hot cell and fuel pool facilities.

Extensive SRPA measurements have been performed on prepared specimens with known concentrations of hydrogen induced in zircaloy specimens provided by GE-GNF and EPRI. Figure 1 shows an SRPA scan for a 3,000 ppm hydrogen Zircaloy-2 specimen. Results of the hydride specimen measurements indicate that the SRPA system is sensitive to hydrogen concentrations <75 ppm and $\geq$3,000 ppm with uncertainties less than 1%. Further, as shown in the figure, the damage to the zircaloy atomic structure is not uniformly distributed on the surface of the plate and indicates that the hydride attack on the surface results in areas of higher and lower hydride damage to the plate.

Figure 2 shows the SRPA-based microstrain measurement system developed for assessing the effects of strain on the atomic structure of zircaloy and the relative effect of strain versus hydride effects on the microstructure of the zircaloy.

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[1] General Electric-Global Nuclear Fuels

[2] Idaho State University
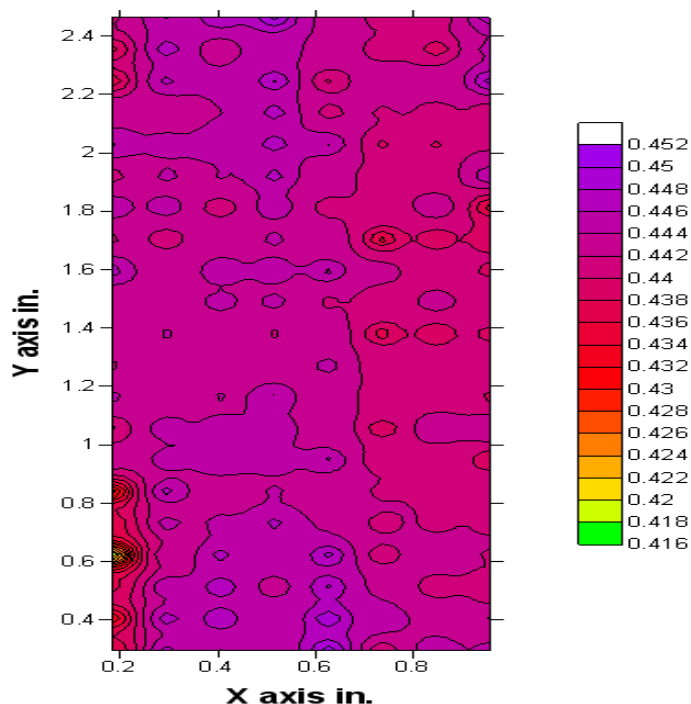
FIGURE 1. SRPA analysis (3000 ppm hydrogen).
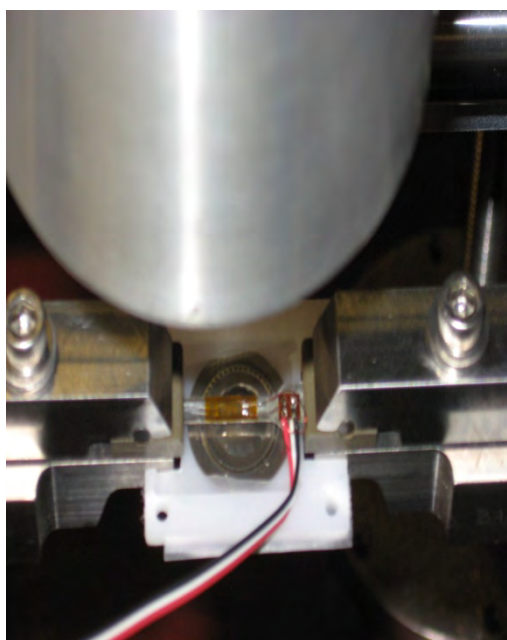
FIGURE 2. SRPA microstrain measurement system.

The SRPA microstrain measurement system allows in situ SRPA measurements of strain while the specimen is under load. The system has been demonstrated to provide direct measurement of strain effects as low as 0.05% strain. Induced strain effects in GE zircaloy components produce a much less significant effect on the zircaloy microstructure than the effect of the induced hydrides.

We developed a specialized radiation-hardened SRPA system that is suitable for measuring irradiated zircaloy specimens and for use in a hot cell environment. This system is designed to allow collimated detector SRPA measurements to be performed on high radiation field specimens. Figure 3 shows the SRPA system being implemented at GE-GNF Vallecitos and Figure 4 shows the conceptual design of the hot cell scanner system to be used in a hot cell with highly-irradiated specimens containing hydrogen or other types of cladding or fuel damage.

In addition to the scanning systems shown, we developed an initial conceptual design of a pool-side SRPA scanning system for use on intact fuel assemblies and other components. This system is considered to be of importance not only to GE-GNF but to EPRI for use at reactor sites world-wide. Initial work has begun with GE-GNF on integrating the physics measurement systems with current pool scanning systems in use at GE facilities.

Benefits to DOE

Implementation of the SRPA measurement system with GE-GNF through the INL CRADA process addresses a number of the current critical issues for the U.S. nuclear power industry and demonstrates a good government/ commercial partnership and the use of "science-based" research to address real world problems. Other DOE missions that could benefit from this program include LWR sustainability, characterization of advanced irradiated fuels for the Reduced Enrichment for Research and Test Reactors and Advanced Fuel Cycle mission area. This project supports the INL and DOE mission of supporting the development of current and future reactor fuels optimized reactor systems. Further it provides capabilities for the development of new reactor fuels and in the minimization of wastes by extending the life of fuels.

FIGURE 3. SRPA rad-hardened scan bed with two detectors.

FIGURE 4. SRPA hot cell scanner conceptual design.

Relevant Publications and Presentations

No peer-reviewed publications have been submitted to date because the project and its results are subject to a non-disclosure agreement with GE-GNF. It is expected that in the upcoming year some publications without proprietary information may be approved by GE-GNF.

Akers, D.W., et al., SRPA Hydride Research and Results (proprietary), GE Vallecitos, July 26, 2011.

Akers, D.W., et al., SRPA Hydride Research and Results (proprietary), GE Wilmington, August 13, 2011.

Akers, D.W., SRPA Hydride Research Overview (nonproprietary), EPRI and PNNL, September 7, 2011.

Akers, D.W., SRPA Hydride Research Overview (proprietary), GE, November 2012.

Advanced Modeling and Simulation Concepts for ATR

Richard Martineau, Ray Berry, David Nigg, Kord Smith,[1] and Barry Ganapol[2]
11-061

The over-reaching goal of this project is to develop the multiphysics modeling and simulation methodology necessary to predict the behavior of the highly heterogeneous and complex three-dimensional geometric configuration of the INL's ATR. Accomplishing this goal will require the development and application of advanced, implicit numerical algorithms for nonlinearly coupled power profile and multiphase conjugate heat transfer. There are three main development deliverables for this LDRD:

1. Development and implementation of the 7-equation two-phase flow model into a MOOSE-based application, called BIGHORN

2. Development and implementation of a strongly coupled conjugate heat transfer algorithm into BIGHORN

3. Development and implementation of a nonlinear diffusion acceleration approach to couple a power profile solution to the conjugate heat transfer into a MOOSE–based application, called Rattle*S*Nake.

Summary

7-Equation, Two-phase Model Implementation in MOOSE. Because of the broad spectrum of phenomena occurring in light water nuclear reactor coolant flows, it is imperative that models accurately describe compressible multiphase flow with multiple velocities, and that the models be well-posed and unconditionally hyperbolic. To meet this criterion, we have adopted the 7-equation two-phase flow model. This 7-equation system was implemented into a MOOSE-based application, called BIGHORN, through a 6-step progression designed to go successively from single-phase compressible flow in a duct of spatially varying cross-sectional area to the compressible, two-phase flow with full thermodynamic and mechanical nonequilibrium. The continuous finite element method requires stabilization for first order hyperbolic equations. A new stabilization method, an entropy viscosity approach, was utilized. A unique attribute of this approach to stabilization of the numerical method is the avoidance of the use of expensive limiters and non-oscillatory reconstructions by the addition of a "smart" degenerate nonlinear dissipation to the numerical discretization of this

equation system. The viscosity coefficient is based on the local size of an entropy production. Our implementation of this promising approach is currently undergoing further development, testing, and evaluation. (Multiple journal articles are in preparation documenting the implementation of this model.)

Tightly Coupled Conjugate Heat Transfer.
The stated goal of this LDRD is to develop the multiphysics modeling and simulation methodology necessary to predict the behavior of the highly heterogeneous and complex three-dimensional geometric configuration of the INL's ATR. Accomplishing this goal will require the development and application of advanced, implicit numerical algorithms for nonlinearly coupled power profile (heat source) and multiphase conjugate heat transfer. The term conjugate heat transfer is used to define the thermal interaction between sub-domains of fluid and solid phases. Across these sub-domain interfaces, the heat flux is continuous and results in variations of temperature within solids and fluids, due to heat conduction between the solids and fluids. A typical example is the heating or cooling of fuel pins and assemblies immersed in flowing reactor coolant. Here, we are using the Mortar Finite Element Method (FEM) to strongly enforce the continuous heat flux from the solid phase heat conduction in the fuel clad, through the solid-fluid interface, and into the thermal boundary layer of the fluid. The Mortar FEM is based upon the Lagrange Multiplier method and discretized with the FEM, where the Lagrange multipliers are used to drive a set of constraints to zero. In this case, the heat flux on both sides of the solid-fluid interface must be equal in an integrated surface integral. We have developed a new, fully implicit Mortar FEM and tested the solution approach in one dimension. Extension to multi-dimensions is the next step. This is a significant step as multi-dimensional sub-domain mesh projections can be quite complicated.

Nonlinear Diffusion Acceleration (NDA) for Multiphysics. The seven-dimensional, Boltzman neutron transport equation (3 in space, 2 in angle, 1 in energy, and 1 in time) poses a challenge for modeling and simulation. Nonlinear Diffusion Acceleration (NDA) is an efficient way to treat the angular variable on solving the transport equation. It introduces a low-order diffusion equation with a nonlinear closure term so that the low-order solution preserves the high-order transport accuracy. The major

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transport calculations are then carried with the low-order equation. Thus, a much fewer number of unknowns are required so that the computing effort can be significantly reduced. We have implemented the NDA in RattleSNake (multi-group radiation S_N transport with continuous Finite Element Method for the formulation of self-adjoint angular flux), a MOOSE-based radiation transport application. The consistent transport-corrected diffusion weak form, including a drift term, has been derived rigorously from the variational argument. This consistent diffusion weak form also takes into account an innovative void treatment of the transport weak form. The streaming and collision operator for each energy group and each direction is inverted with the multi-grid sweep for the transport correction. The implementation has been tested with several benchmark problems. The spectral radius of the nonlinear iteration is demonstrated to be less than 0.5 in the full range of cell thickness in term of neutron mean free path with a one-group homogeneous problem. For the KAIST-3A benchmark, a seven-group pin-homogenized problem with relative strong transport effects, the error in k-effective can be reduced less than 1 pcm with 7 iterations. The fully converged solution is exactly equal to the solution of the direct transport solve, as we expected. Further optimizations with a more realistic problem with a number of elements and groups needs to be done in the future. Currently the diffusion scheme has the same number of energy groups, mesh, and spatial order as the transport scheme.

Currently RattleSNake mainly uses the Jacobian-Free Newton Krylov (JFNK) method with nonlinear elimination of the eigenvalue constraint equation to solve the transport eigenvalue problems. This method requires several free power iterations to assure the Newton iteration con verges to the fundamental mode before the nonlinear steps. Although the minimum number of the free power iterations is problem dependent, usually five is a good guess to start with and it is not hard to apply the trial-and-error method to figure it out. We can always put more power iterations to be conservative. The nonlinear elimination is critical to the success of the method with which the eigenvalue is updated every linear iteration in the nonlinear step. This method reduces the number of nonlinear iterations significantly comparing with the equivalent number of power iterations of the traditional power method. However, it still requires a number of linear iterations of the transport system due to the fact of the

presence of the scattering and the fission. Residual evaluation and preconditioning of the transport system are costly.

NDA, or what is commonly known as Coarse-Mesh Finite Difference, has been applied to solve the transport eigenvalue problem. Because the lower-order diffusion equation can be solved on the same spatial mesh of the transport equation, we will use the terminology NDA exclusively in this report. The advantage of doing NDA can be seen in the fact that only the streaming and collision operator of the transport equation needs to be inverted for the transport update. This inversion can be done group by group and direction by direction independently. With the first-order transport approach, this inversion is done efficiently with the well-known transport sweep. With SAAF-SN-CFEM adapted by RattleSNake, the inversion can also be done efficiently with the multigrid sweep. Traditionally, NDA is implemented in the fashion of the fixed-point iteration, i.e., iteration upon the full diffusion solve and the transport update. Fourier convergence analysis has been conducted and proves the fast convergence of the fixed-point NDA. However, if the lower-order diffusion discretization scheme is inconsistent with the transport scheme, instability could happen. Applying NDA together with the JFNK method can be a remedy to restore the stability. Because a consistent diffusion scheme is designed rigorously with the variational derivation in RattleSNake, we do not have such instability issues. We have the freedom to choose either the fixed-point iteration or the JFNK approach.

Benefits to DOE

This LDRD is part of a long-term goal of using ATR as a platform for verification and validation of advanced modeling and simulation and as a tool for Light Water Reactor performance enhancement. As such, this project directly contributes to DOE-NE and DOE's mission for energy security. Successful completion of this necessary, advanced proof of principal LDRD will allow optimal transition to programmatic funding under the ATR Life Extension Program.

Relevant Publications and Presentations

Wang, Y., H. Zhang, and R. Martineau, "Diffusion Acceleration Schemes for the Self-Adjoint Angular Flux Formulation with a Void Treatment," *Nuclear Science and Engineering.* (submitted)

Kadioglu, S., R. Berry, and R. Martineau, "A Point Implicit Time Integration Technique for Slow Transient Flow Problems," *Journal of Computational Physics.* (submitted)

"Multi-scaled, Two-phase Flow Modeling Directions for Light Water Nuclear Reactors," *Thermal-hydraulics of Nuclear Systems short course, Bethesda, MD*.

Full-Scope Human System Simulation Laboratory for Plant-Specific and Generic NPP Simulator Models Studies

Jacques Hugo, David Gertman, and Ronald Boring
11-062

Characterizing control room operator performance in the presence of changing technology is a significant challenge for the DOE, the Nuclear Regulatory Commission (NRC), and the U.S. nuclear industry. In many ways, advanced technology available today is driving the changes being proposed for existing and advanced reactor control room designs. However, the technical basis, that is, data for determining the efficacy of human performance under these conditions, is largely absent. Currently, the Human System Simulation Laboratory (HSSL) at INL is the only test bed facility in the DOE complex for the evaluation of various aspects of human performance and human system interaction for proposed reactor designs and upgrades, including staffing levels, situation awareness, and operator interface design. However, in its current state the HSSL is still immature and its ability to support future DOE missions is limited, specifically in the assessment and improvement of human performance under normal and emergency situations in control rooms, remote shutdown stations, technical support centers, maintenance outage control centers, and other environments where humans interact with complex technology.

This project supported the expansion of INL's existing control room simulator infrastructure and core capability to support unique state-of-the-art human factors studies in advanced control room environments. This includes the development of a standard comprehensive set of human performance measures for human-in-the-loop studies, the design and evaluation of advanced human-system interface technologies, and methods that can be applied to the resolution of challenges in the area of staffing for multiple reactors, workload, situation awareness, and alarm management strategies in nuclear power plant (NPP) control rooms.

Supporting research conducted under this LDRD included:

- Development of a human factors research capability that would enable experimentation in controlled settings representative of generic as well as specific industry conditions and requirements

- Implementation of NPP simulator models that are representative of the most important technologies being employed in the U.S. including small modular and light water reactors

- Identifying or developing tools and methods necessary for research within this environment

- Designing, developing and testing advanced human-system interaction technologies and methods.

Current and next generation control rooms present many challenges to the optimization of human performance, productivity, safety, and well-being. Many of these challenges are poorly understood due to a lack of adequate and suitable research facilities and empirical studies. This project offered the capability for unprecedented human factors and human-system interface research that will address novel control rooms for advanced plants, control room upgrades for existing plants, and safety certification of advanced control room concepts from the perspective of optimizing control room design to support operator performance.

Summary

The two phases of the project focused on developing the technical and procedural requirements to establish a basic system architecture that would enable human factors researchers to conduct human performance experiments with power plant simulations. These requirements were validated by performing a range of experiments with the simulators and test equipment mentioned previously. This validation specifically focused on the extent to which the available systems provided an acceptable approximation of actual control room environments. Special consideration was given to R&D needs and specifications were developed to equip the HSSL to simulate a complete set of benchboard panels for a specific plant control room, or for generic pressurized water reactor simulations (Figure 1). This configuration allows full-scale simulation of a control room, which makes the HSSL the only one of its kind in the world and will allow research and experimentation that cannot be done anywhere else (Figure 2).

FIGURE 1. Touch screen benchboard panels.

FIGURE 2. New HSSL configuration at EROB.

The evolution of the HSSL is ongoing and the next phase will focus on refining the human factors laboratory methodologies. This includes requirements for upgrading the human performance measurement suite with additional eye tracking and cognitive performance measurement equipment, updated participant observation software, and improved prototyping software. The refined specifications will provide information needed to equip the HSSL for more extensive research.

Benefits to DOE

The capability developed supports the objectives of DOE and ultimately several sectors of the nuclear industry. This enables INL to provide all stakeholders with research-based, empirically determined guidance on the performance of operating crews and the human contribution to system resilience under various task and environmental conditions. In particular, this LDRD supports proof-of-principle demonstration of the HSSL and offers

R&D opportunities for specific human factors and technology analyses, evaluation of state-of-the-art human-system interaction technologies to support operator decision-making and situation awareness, and development and evaluation methods for new concepts of operation of next generation power plant designs.

The HSSL is a unique and vital resource in the INL's research arsenal. Without it, we cannot answer the difficult questions, like, "Can you safely operate more than one power plant unit from a single control room? How many operators do you really need? How will operators maintain situation awareness with advanced technology and increased complexity?" and many more.

With the advanced display panels described above, the HSSL now offers a near-realistic reconfigurable control room simulator that provides a much-needed capability for instrumentation and control (I&C) and human factors research, including development of operator-centric design requirements, behavioral and performance testing, such as the role of operator limitations, mental models, perception and cognition in human-system interaction.

Finally, the R&D activities established DOE in a leadership role for advanced visualization, human-in-the-loop simulator studies, cognitive studies, and the empirical testing and validation of advanced design approaches.

Relevant Publications and Presentations

Hugo, J., K. Le Blanc, and D. Gertman, "The Development of a Human Systems Simulation Laboratory: Strategic Direction," *Proceedings of the Eighth American Nuclear Society International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human-Machine Interface Technologies, NPIC&HMIT 2012, San Diego, CA, July 23–26, 2012.*

Hugo, J. and D. Gertman, "The Use of Computational Human Performance Modeling as Task Analysis Tool," *Proceedings of the Eighth American Nuclear Society International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human-Machine Interface Technologies, NPIC&HMIT 2012, San Diego, CA, July 23–26, 2012.*

Hugo, J., "Computational Human Performance Modeling for Alarm System Design," *Proceedings of the Eighth American Nuclear Society International Topical Meeting on Nuclear Plant Instrumentation, Control, and Human-Machine Interface Technologies, NPIC&HMIT 2012, San Diego, CA, July 23–26, 2012.*

Hugo, J., "Human System Simulation Laboratory: Capabilities and Build-out Plan," *Presentation to Peer Review group, Idaho Falls, ID, April 2012.*

Hugo, J., "Human System Simulation Laboratory: HSSL Plan, Capabilities and Build-out Plan," *Presentation to the Joint Advanced II&C Technologies Utility Working Group Workshop, Phoenix, AZ, May 2012.*

2-D and 3-D EBSD Technique Development and Microstructure Reconstruction for Phase Field Microstructure Evolution Models

Melissa Teague, Michael Tonks, Stephen Sintay,[1] and Brian Gorman[2]
12-031

Electron back-scatter diffraction (EBSD) scans provide detailed description of a microstructure that can be reconstructed to define initial microstructures for mesoscale models. While reconstruction methods exist for collecting EBSD scans from non-radiological samples, method development is needed to perform these types of experiments on radiological samples. Additionally, no current method exists for using these reconstructed 2-D and 3-D microstructures in phase field models, a deficiency that will be addressed by this LDRD project. This project aims to develop a method to reconstruct realistic microstructures from EBSD scans of un-irradiated and irradiated uranium dioxide (UO_2) and Zircaloy cladding for use in INL's finite element-based phase field code MARMOT. The project will develop experimental techniques for collecting 2-D and 3-D EBSD data from radiological samples and the methodology to reconstruct and import this data directly into mesoscale phase-field models.

Summary

A focused ion beam, along with its attached EBSD detector, was used to characterize 3-D microstructure and chemistry of irradiated oxide fuel. Both the ability to serial section and perform EBSD on irradiated fuel are unique first-of-its-kind research performed at INL and several journal articles are expected from this work. Having the ability to study the crystal structure, chemistry, and microstructure of irradiated fuel in 3-D is critical to understanding the fundamentals of fuel performance.

The framework was developed to reconstruct 2-D structural data obtained from these experiments for use in INL's mesoscale code MARMOT. Preliminary models of fission gas evolution have been developed using the reconstructed microstructure (Figure 1).

An INL employee, Brad Fromm, has been hired through this project who brings a strong background in microstructure reconstruction and EBSD experimental practice to the laboratory. The LDRD will support the research for the student's Ph.D. through Washington State University. The Ph.D. student will develop methods for 3-D reconstruction of microstructures in MARMOT. He will also develop methods to create statistically similar microstructures. On the experimental side, he will work with the PIs to develop improved sample preparation methods for use with the EBSD detector.
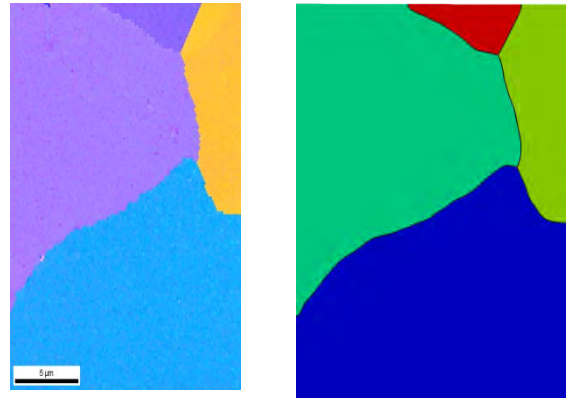
FIGURE 1. Microstructure reconstruction in MARMOT of a high burnup MOX fuel, where the EBSD scan is shown on the left and the reconstruction is shown on the right.

Benefits to DOE

DOE benefits from the project by the development of unique industry-leading capability to analyze radiological materials utilizing 2-D and 3-D EBSD as well as the ability to utilize this experimental information in phase field models. The capability to examine radiological samples with advanced characterization techniques such as EBSD is critical to understanding of current fuel performance and behavior spent nuclear fuel storage. The ability to reconstruct the experimental data and utilize in-phase field modeling efforts provides critical synergy between experimental efforts and lower length-scale modeling.

Relevant Publications and Presentations

Teague, M., B. Gorman, S. Hayes, and J. Carmack, "Microstructural and Chemical Characterization of High Burn-up Mixed Oxide Fuel," *Presented at TMS 2012, Orlando, FL, March 11–15, 2012*.

Tonks, M.R., D.R. Gaston, P.C. Millett, R.L. Williamson, C. Stanek, and D. Andersson, "Multiscale Fuel Performance Modeling: Coupling Atomistic, Meso- and Continuum Scale Simulations," *ANS, Chicago, IL, June 25–28, 2012*.

[1] Los Alamos National Laboratory

[2] Colorado School of Mines

Development of an Uncertainty Quantification Method for MIR Facility

Piyush Sabharwall, Hugh McIlroy, Carl Stoots, Barton Smith,[1] and Pavlos Vlachos[2]
12-045

Currently, Computational Fluid Dynamics (CFD) is widely used in the nuclear thermal hydraulics field for design and safety analyses. However, validation of this method is still an unresolved issue. In order to validate CFD codes, high quality multidimensional flow field data is essential. The Matched-Index-of-Refraction (MIR) Flow Facility at INL has a unique capability to contribute to the development of validated CFD codes through the use of Particle Image Velocimetry (PIV). The significance of the MIR facility is that it permits nonintrusive velocity measurement techniques, such as PIV, through complex models without requiring probes and other instrumentation that disturb the flow. The MIR was modeled after a typical wind tunnel, and was fabricated with a stainless steel frame. The facility consists of several components, including a settling chamber, square contraction, and test section.

In the MIR facility, uncertainty quantification is a challenging task due to the use of optical measurement techniques. This study is developing a reliable method to analyze uncertainty and sensitivity of the measured data and develop a computer code to automatically analyze the uncertainty/sensitivity of the measured data.

The main objective of this study is to develop a well-established uncertainty quantification method for the MIR Flow Facility, which consists of many complicated uncertainty factors. In this study, the uncertainty sources are being resolved in depth by categorizing them into uncertainties from the MIR flow loop and PIV system (including particle motion, image distortion, and data processing). Then, each uncertainty source is mathematically modeled or adequately defined. Finally, this study will provide a method and procedure to quantify the experimental uncertainty in the MIR Flow Facility with sample test results. This study is led by INL researchers and includes participation by graduate student researchers, academia and industry for high-end PIV data collection and analysis in order to resolve the many technical challenges in estimating PIV uncertainty. The uncertainty quantification method developed in this study will lead to high quality MIR data with accurate and reliable uncertainty quantification and it will be a tremendous asset to the ongoing efforts to validate advanced computational methods.

Summary

The main technical benefit of this effort is to significantly improve data quality of the MIR facility, and the sensitivity study will dramatically improve the ability of the MIR/PIV technique to collect high-quality data with less effort by concentrating on important parameters. It will make the whole experimental process in the MIR facility much more efficient and productive.

The MIR facility has tremendous potential as a user facility for basic and applied research by government, industry and academia where accurate and reliable uncertainty quantification is essential for producing high-quality data for computer code validation.

Despite extensive research in this area there is no accepted methodology for quantifying the uncertainty associated with individual vector evaluations. The PIV measurement uncertainty is affected by the numerous elements present in the instrumentation chain, and in the vast majority of the cases those uncertainties are interconnected and coupled.

The main objective for FY 2012 was to develop and test uncertainty estimation techniques based on uncertainty surface method, shown in Figure 1 and correlation plane method, shown in Figure 2 with the help of Utah State University and Virginia Tech University, which are both team members for this project. So far these methodologies have been applied to synthetic data sets with excellent results. Now, both methodologies are being compared with each other for a given experimental data set.

During the second year of this project we will build upon the methods, tools and infrastructure developed during year one to extend the PIV uncertainty quantification methodology to three-component stereoscopic measurements. The Utah State University team will pursue a method to combine random uncertainties for 2-component velocity fields (which were developed in year one) with stereo bias uncertainties, specifically for a stereo method based on de-warped images. This is the stereo method used in the LaVision DaVis PIV software. The Virginia Tech team will pursue a method to combine random uncertainties for 2-component velocity fields (which were developed in year one) with stereo bias uncertainties, for a stereo method based on stereo reconstruction of the measured planar velocity fields.

[1] Utah State University

[2] Virginia Tech University

Fluid dynamics and turbulence is still one of the most challenging topics in the engineering field because of their large uncertainty. The proposed study will support understanding by investigating fundamental fluid dynamics through improving the quality of data from the MIR facility and PIV technique.
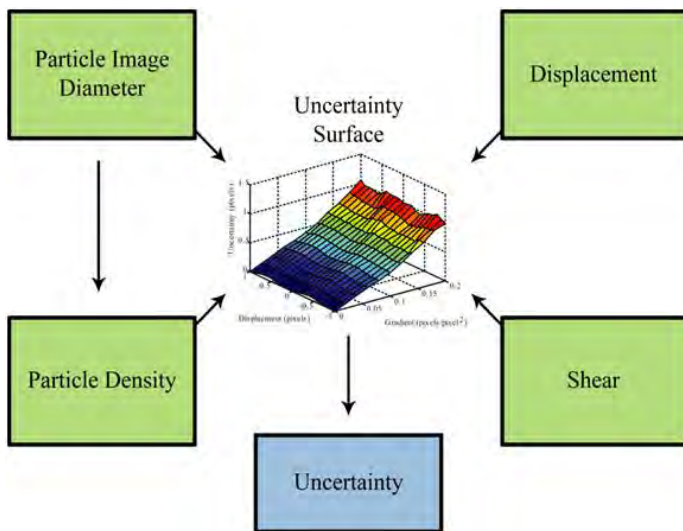
FIGURE 1. Uncertainty Surface Method.
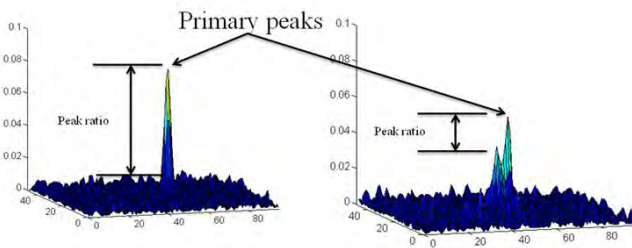
FIGURE 2. Estimation of Uncertainty Bounds for Individual PIV Measurements from the correlation plane, (Virginia Tech University).

Benefits to DOE

This work will contribute to the DOE mission by working to quantify PIV uncertainty that can be used to ensure high quality data for the validation of CFD codes that will be used for nuclear reactor design and safety analysis. Additionally, this work will directly contribute to the accomplishment of DOE goals by helping to develop the CFD tools necessary for NE programs and by helping to

develop and characterize PIV uncertainty estimates that can be used to validate advanced computer codes.

Relevant Publications and Presentations

Sabharwall, P., T. Conder, R. Skifton, C. Stoots, B. Smith, P.P. Vlachos, and J. Charonko, "PIV Uncertainty Methodologies for Matched Index of Refraction Facility," *Proceedings of the ASME 2013 Summer Heat Transfer Conference, Minneapolis, July 14-19, 2013.* (submitted)

Charonko, J. and P.P. Vlachos, "Estimation of Uncertainty Bounds for Individual PIV Measurements From Cross Correlation Peak-Ratio," *Meas. Science and Tech.,* October 2012. (submitted)

Charonko, J. and P.P. Vlachos, "Estimation of Uncertainty Bounds from Cross Correlation Peak Ratio for Individual PIV Measurements," *Proceedings of 2012 ASME FEDSM,* FEDSM2012-72475, *July 8-12, 2012, Puerto Rico.*

Charonko, J. and P.P. Vlachos, "Estimation of Uncertainty Bounds for Individual PIV Measurements," *64th Meeting of the APS Division of Fluid Dynamics, November 20-22, 2011, Baltimore, MD.*

Charonko, J. and P.P. Vlachos, "The Effect of Velocity Dynamic Range: Direct Uncertainty Estimation from Cross-Correlation Signal to Noise Ratio," *PIV Uncertainty Workshop, May 11-13, 2011, Las Vegas, NV.*

Warner, S.O. and B.L. Smith, "Autocorrelation-Based Estimate of Particle Image Density for Diffraction Limited Particles," *Meas. Science and Tech.,* December 2012. (submitted)

Warner, S.O., B.L. Smith, and P.P. Vlachos, "Autocorrelation Based Estimate Of Particle Image Density In PIV," *Bull. Am. Phys. Soc.* 57, 2012.

Warner, S.O., MS Thesis, "Autocorrelation Based Estimate of Particle Image Density in PIV*," Utah State University, November 2012.*

"Development of an Uncertainty Quantification Method for MIR Facility," *Presentation to Idaho National Laboratory Peer Review Committee Members, Idaho Falls, Idaho, June 20, 2012.*

Development of a High Burnup Zr-Based Fuel Cladding for LWRs

Robert Mariani, James Cole, and Randall Fielding
12-061

A new oxide dispersion-strengthened (ODS) Zr-based alloy is sought for improved safety, reliability, and burnup in Light Water Reactor (LWR) applications. However, ODS alloys have high prices that arise from traditional mechanical alloying that involves energy-intensive, time-consuming, and labor-intensive processes. To be cost-effective, an ODS Zr-based cladding alloy would therefore require new materials and methods that eliminate traditional powder metallurgical methods. Novel ODS agents were conceived that could be used in a way that eliminates traditional powder metallurgy processes, such as mechanical alloying, permits large batch and/or continuous castings, and permits conventional welding.

Proposed material additions to the Zr alloy are based on thermodynamics, experimental data, a simple transport model, and prior modeling experience with other ODS-type materials. Niobium (Ta or V) is added for its property in which the hydrogen permeability increases with decreasing temperatures, thereby avoiding or mitigating hydride precipitation. A second additive such as molybdenum (Mo) may be used, but may not be needed, at a level to induce phase-segregation of niobium (Nb) from the bulk Zr and induce Nb precipitation on grain boundaries (since Nb is soluble in Zr), which helps prevent increasing hydride levels with thermal cycling. A third additive, such as Y_2O_3, is used to control grain-size and inhibit microstructural changes to the cladding that can result from irradiation at elevated temperature and thermal cycling with outages. The third additive (e.g., Y_2O_3) can also facilitate rapid formation of the more mechanically stable cubic ZrO_2 corrosion layer on the cladding, as compared to its other phases.

The initial focus of the research effort is development of the nano-scale ODS agents for alloy fabrication. A contract with a small business was established to produce, for the first time ever, nano-spheres of Mo (in two size ranges) with a nano-scale coating of yttria (in two ranges of weight fraction). To date, the nano-scale Mo cores have been produced. In the future, after the desired materials characteristics have been verified, the ODS agents will be processed using conventional alloying methods (such as induction melting with a stir cycle) and traditional ODS powder metallurgical methods for comparison. Also, the inverted structure will be attempted, with yttria cores having a coating of Mo metal (or another metal).

This technology offers improved performance and reliability for the current fleet of nuclear power plants, with potential for increased burnup, uprates, and safety margin for wet and dry storage. Applications of this research are much broader than Zr-based alloys, and include Fe-based alloys for extreme service involving high temperatures and corrosive environments that require resistance to thermal cycling fatigue, creep deformation, and surface wear. As a result, the cross-cutting applications within DOE (for example, Emerging Technologies) hold high potential for significant advances in science, technology, and energy-savings for ODS alloy production and hold significant commercial value.

Summary

A subcontract was established for the preparation of novel, specialty nano-scale materials to be used as ODS agents for Zr-based alloys. The technical approach is described in the specification for the patent application [U.S. Patent Application No. 13/021,480]. The first procurement of ODS agents is intended to show proof-of-principle for producing custom, compounded, nano-scale ODS agents with a range of size characteristics (four compound preparations are being procured). To date, nanoscopic molybdenum cores have been produced.

Literature was reviewed for application of the technology to Fe-based alloys and steels, and certain materials were identified as candidate ODS agents in this expanded application. Their candidacy was further corroborated using a thermodynamic software package. Significantly, the application of these particular candidate materials is expected to allow conventional welding of ODS steels, based on tunable physical properties for the nano-scale dispersoids. An invention disclosure record was submitted for the application of the zirconium-alloy technology to the Fe-based alloys and steels.

A federal business opportunity announcement was made to solicit industrial partners. We signed a non-disclosure agreement with one company. INL submitted the information and the potential partner declined participation as the results were too preliminary for their interests. However, it was admitted that if the ODS agents can be prepared to give the desired properties, the ODS agents will enable the overall technology.

Benefits to DOE

This research aims to deliver Zr-based alloys resistant to creep and hydriding in LWR applications, offering higher burnups, uprates, and improved safety margins for wet and dry storage. New materials offer new fabrication methods for ODS alloy that eliminate time-consuming, labor- and energy-intensive traditional methods such as mechanical alloying. The research initially focuses on zirconium-based cladding applications and improvements would increase understanding of Zr-alloys for LWR applications. The materials and process approach have already been adapted for application to iron-based alloys and steels with suitable modification of the ODS precursor agents, with a reasonable expectation that conventional welding may be employed. Broad application of this technology would overcome a 100-year old science and technology barrier, would bring significant energy-savings in the production of ODS alloys, and would pose possibly tremendous commercial value as applied to steels. Specific benefits to the DOE include developments in materials science, engineering, manufacturing, and welding and developments in LWR cladding and iron-based alloys for high-temperature, extreme service applications. Economic benefits and lesser energy requirements can be foreseen in manufacturing and welding and in longer service life of components.

Relevant Publications and Presentations

None.

Development of Diamond-Based Sensors for User Facility Capabilities at INL Advanced Test Reactor

David Chichester, James Johnson, and Gordon Kohse[1]
12-062

The project is assessing the operating characteristics of chemical vapor deposited (CVD) diamond-based sensors for use as in-core neutron monitors in support of ATR NSUF research activities. Current state-of-the-art, real-time, in-core neutron flux monitoring uses either self-powered neutron detectors (SPNDs) or fission chambers. If the CVD-diamond neutron detectors perform as we hypothesize they will be more reliable and stable than SPNDs, have larger dynamic ranges than SPNDs, and be less expensive/easier to handle than fission chambers. Also, their lower cost may avoid the need to reuse these detectors and allow them to be used in greater numbers for instrumented experiments.

Summary

The goal for this fiscal year was to experimentally study the performance of CVD carbon-diamond film semiconductor radiation detectors for use as multi-energy neutron detectors. The project started with a small review to determine the important design specifications needed to acquire a first set of CVD-diamond neutron detectors. Following this, an order was placed to purchase prototype detectors, which were received at INL in the second quarter of FY 2012.

Upon receiving the detectors we began evaluating their performance, using on-hand electronic data acquisition equipment and radiation sources available at INL's North Yellowstone Complex Laboratory and the Active Neutron Interrogation Laboratory. In June an intern, Ms. Mareena Robinson, joined the research project. Ms. Robinson is a second-year graduate student in Nuclear Science Engineering from the Massachusetts Institute of Technology (MIT). In July the research team travelled to MIT to perform a week-long measurement campaign at the MIT research reactor. At the reactor we used some specialized alpha-emitting radioisotope sources and the thermal-neutron beam port from the reactor. We are now working to interpret this data.

Based on initial tests at INL using calibrated ^{252}Cf neutron sources (see Figure 1) we have determined that for fast neutrons in the energy range of fission-spectrum neutrons the detectors (4 mm $\times$ 4 mm active area) have an intrinsic efficiency of approximately $(3.0 \pm 0.2) \times 10^{-7}$ %. Further, this signal is separable from the CVD-diamond detector thermal-neutron response. This indicates that the detectors may be able to provide multi-energy spectral information when used inside the high-flux environment of a materials testing reactor such as ATR.

At MIT the thermal-neutron beam port from the MIT research reactor time-of-flight (TOF) station was used to perform neutron spectroscopy measurements and to allow determination of the thermal neutron efficiency of the detectors. The motivation for the TOF experimentation was to categorize the energies of the neutrons incident on the detector from the beam. The beam track was 1.5-m-long with a cadmium chopper wheel at the far end of the track, in front of the beam-port shutter. The chopper wheel created a pulsed beam with a frequency of 500 Hz with pulse periods of 2 ms; this served as the start for TOF acquisition. Measurements were taken at a close position of 0.083 m and the far position of 1.219 m from the chopper wheel. The stop pulse for the TOF acquisition was generated when a neutron was detected inside the CVD-diamond detector. An optical signal was generated at the time the chopper wheel opened, signaling the beginning of a neutron burst. This signal was read into a constant fraction discriminator (CFD) which ensured the start pulse was trigger at the same time regardless of jitter or amplitude walking. This start trigger was sent into a time-to-amplitude (TAC) converter. The signal from the detector was passed through a preamplifier and split to the CFD and a spectral amplifier. This detector signal was split again to a multichannel analyzer (MCA) and an oscilloscope to monitor the pulses generated. The detector signal passed through the CFD and was used as the stop signal to the TAC. An amplitude pulse was generated from the TAC which is proportional to the time interval between the start and stop pulses. We are currently working to assess the detector's thermal-neutron detection efficiency; prior work in this area has shown similar detectors to have an intrinsic efficiency for detecting thermal neutrons of ~10^{-5}. An example of the signal pulse-height-spectrum from the lithium-coated CVD-diamond detector is shown in Figure 2.

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[1] Massachusetts Institute of Technology
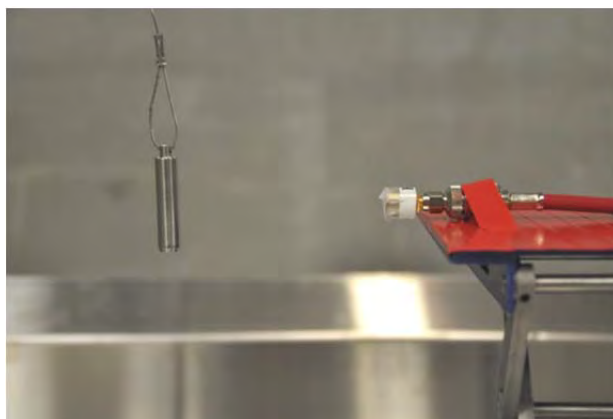
FIGURE 1. The configuration of the ^{252}Cf source and CVD-diamond detector. The left photograph shows the slightly moderated ^{252}Cf source and the CVD-diamond detector. The right photograph shows the bare ^{252}Cf source and the CVD-diamond detector.
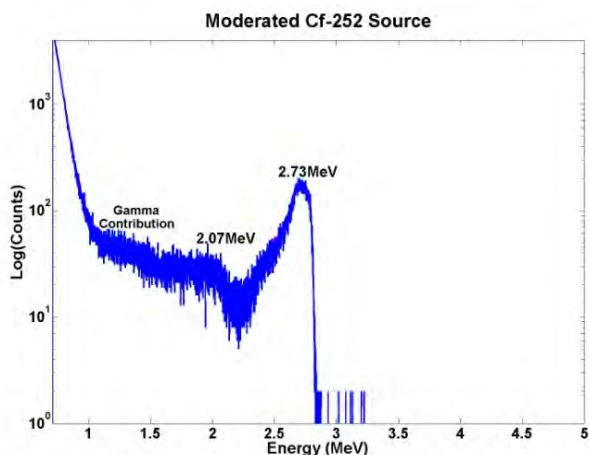
FIGURE 2. This the pulse-height-spectrum captured using the CVD-diamond detector with the moderated ^{252}Cf. The triton peak is located at 2.73-MeV and the alpha continuum starts at 2.07-MeV. Due to its larger size and charge, the alpha particle has a higher interaction probability inside the detector, which can be seen in the broadening of the peak.

As a part of this project, we are working to establish an informal collaboration between INL and researchers at The Italian National Agency for New Technologies, Energy and Sustainable Economic Development and Rome "Tor Vergata" University, both in Italy. Indeed, these partners have agreed to work with us in FY 2013 and to supply us with additional CVD diamond-based sensors. This is a key development for this program. Next year we are planning to further advance this collaboration. These partners have been interested in our work as well, in particular our recent tests performed at the MIT (Massachusetts Institute of Technology) research reactor, because they have not performed these types of measurements themselves.

Benefits to DOE

This project will directly contribute advanced nuclear technology for the next-generation of nuclear power through the development of new neutron flux monitoring tools for use in nuclear fuels and materials research and development. Added benefits may be found with the identification of approaches for using CVD-diamond neutron detectors in Light Water Reactor ex-core or in-core power monitors, in support of Light Water Reactor sustainability programs sponsored by DOE.

Relevant Publications and Presentations

None.

Separate Effects Fuels Development Capability

Keith Jewell, Tony Hill, and Eric Burgett[1]
12-070

Intense Neutron Spectra with Independent Gamma, Hydraulic, and Temperature Separate-effects (INSIGHTS) will allow independent control of the neutron irradiation spectrum, the gamma field at the test sample location, and the isolated application of hydraulic pressure over the entire temperature range expected in current and future reactor designs. The design goal is the capability to deliver an exponential increase in the available data on the time evolution of microstructural changes in fuel samples specifically engineered for isolated effects study. This data can be used in the iterative development of science-based modeling and simulation that is accurately validated and benchmarked against experimental data. The deliverable for FY 2012 was an engineering design report that presents the modeling and simulation effort used to evaluate the feasibility and practicality of the accelerator driven, fuel boosted neutron irradiation facility. The engineering design report details the results from modeling a number of different accelerator, target, and booster fuel designs to arrive at a recommended option for developing the separate effects and testing capability. The three main challenges with the design are: the heating in the accelerator target used to produce the initial neutrons, the heating in the booster fuel used to create the sample irradiation neutrons, and the intensity and spectrum of the neutron flux that can effectively interact with the experimental samples. The engineering design report addresses these three main challenges and presents the base case and optimized design options, taking into account cost, resource availability, fuel fabrication, and licensing concerns. The full engineering design report presents the advantages and disadvantages of various accelerator and fuel options through the detailed modeling and simulation results of the neutronics and heating for the particular design options selected. The report contains complete descriptions of the design constraints, assumptions, accelerator targets, sub-critical irradiation facility, booster fuel types, criticality design and safety, heat load calculations, neutronics, and radiation safety.

Summary

Through a comprehensive modeling and simulation effort in FY 2012, we have concluded that the INSIGHTS separate effects capability is feasible and achievable in the near term. A full engineering design report has been generated outlining the feasibility of the design of INSIGHTS. A comprehensive set of appendices is included with the report outlining all major variations and permutations to the INSIGHTS system. These designs and all subsequent permutations are provided to management for consideration and selection. This report was written without bias to any permutation to provide the maximum flexibility in the selected path forward. The only bias applied in the creation of this document is in the removal of options that do not meet the primary mission of separate effects testing with line of sight access for a wide variety of neutron spectra including fast reactor spectra. The main criteria for removal from consideration is the presence of non-physical phenomena which one would not find in a fast or thermal reactor spectra, namely, high-energy neutrons from spallation neutron sources.

A number of choice candidates have been selected and full design information is presented in the engineering design report. All major considerations have been calculated, and include the ability to: (1) achieve a neutron flux in the primary irradiation chambers of 1×10^{15} n/cm^2/s for a minimum of eight hours a day while maintaining a safe operating environment, (2) cool the accelerator target required for driving INSIGHTS at 1×10^{15} n/cm^2/s with existing technology, (3) cool the subcritical assembly and lead scattering medium required for driving INSIGHTS at 1×10^{15} n/cm^2/s with existing technology, (4) be fabricated from existing technologies capitalizing on assets at INL and Idaho State University, and (5) license the system in the near term (<2 years).

The final proposed design is a high energy, single stage electron photoneutron production target driving U_6Mo fuel. To further improve safety of the system, several features will be added from the other calculated design options to allow greater flexibility and higher heat loads in the future. A continuous wave electron linac is the desired choice. A twelve irradiation chamber system is proposed for the final design. INSIGHTS can drive on as few as four driver fuel assemblies but can utilize up to twelve with lower requirements on initial fuel enrichments. A conical, four coolant loop liquid bismuth cooled target is proposed for the electron photoneutron target. The recommended target is metallic depleted uranium with tungsten copper trapezoidal cooling fins. The four loop cooling system provides redundancy and extra operating tolerance for future incorporation of pulsed systems or higher neutron

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[1] Idaho State University

fluxes in the primary irradiation cavities. In addition, this accelerator-target system can run INSIGHTS ~250% longer than other positive ion machines.

The engineering design report presents a recommended, optimal path forward for realizing a significant advance in the study of microstructural behavior of fuel material under realistic reactor conditions. This capability would bring a science-based understanding of the microstructural, time-dependent phenomena that drives the macroscopic fuel performance, and would be a tremendous complement to the well-established irradiation cycle and post irradiation examination experimental paradigm. A wealth of new information that informs advanced modeling and simulation is, at this time, a feasible and realistic goal for exponential advances in fuels and materials development.

Benefits to DOE

This work supports DOE's mission of energy security by furthering the knowledge of nuclear fuels and materials development—helping to establish a more efficient fuel cycle and contributing to the next generation of nuclear reactors.

Relevant Publications and Presentations

None.

Characterization of Intergranular Corrosion Using Thermal Wave Imaging

Marat Khafizov, Sebastien Teysseyre, and David Hurley
12-080

Intergranular corrosion (IGC) in metal alloys is an important material science problem. IGC leads to stress corrosion cracking in Ni-based alloys used as structural materials in pressurized water nuclear reactors. Current understanding of IGC is limited due to the absence of experimental in situ methods. Electron microscopy techniques are widely used to characterize the microstructure resulting from intergranular particle diffusion. Unfortunately these destructive techniques do not allow in situ observation and only provide a snapshot of the complex dynamical process. To provide better understanding of the mechanisms of corrosion kinetics we are working to develop a laser-based instrument capable of in situ characterization.

Laser-based thermal wave imaging (TWI) is a nondestructive technique typically used to study thermal properties of materials. The thermal wave profile generated by the heating laser depends on the constituent's bulk thermal properties, and most importantly for this work, thermal resistance across internal interfaces. A discontinuity in the crystalline structure acts as a barrier to heat transport. The amount of thermal resistance depends on the morphology of the interface determined by crystallite misorientation on the either side of the interface, interface roughness, and impurity segregations. We postulate that ongoing IGC results in dynamic thermal resistance across the grain boundary and TWI can be applied to measure the IGC in real time.

Summary

Our experimental approach is based on modulated thermoreflectance. An amplitude modulated pump beam excites thermal waves within the sample and small temperature induced reflectivity changes are detected using a probe laser. Tightly focused beams allow detection of submicron thermal features. We have explored three different modes for detection.

The first is a simple optical approach that requires only a single laser beam measurement where the optical reflectivity profile of the surface is analyzed. Its rapid turnaround makes it suitable for initial detection of possible grain boundary oxidation. However, this approach is sensitive to surface imperfections and does not provide sufficient means to quantify the thermal properties of an interface.

The second mode, involving thermal wave imaging, implements a configuration where the pump and probe are collinearly aligned and the sample is scanned. The thermal signal in a region removed from an oxidized grain boundary has a constant value. However, the response in the vicinity of an interface is perturbed, as shown in Figure 1. When the beams are away from an interface, the thermal signal is constant. In the vicinity of an interface, the thermal signal deviates from a constant value. An interface with high thermal resistance is needed to distinguish the signal associated with a grain boundary from noise. The higher thermal resistance of an oxidized grain boundary results in slower dissipation of heat and thus a larger phase lag close to the interface. This approach alone is not sufficient to unambiguously identify a discontinuity in the signal as due to oxidation. Surface roughness associated with preferential etching near a grain boundary will result in a parasitic signal due to excessive light scattering.
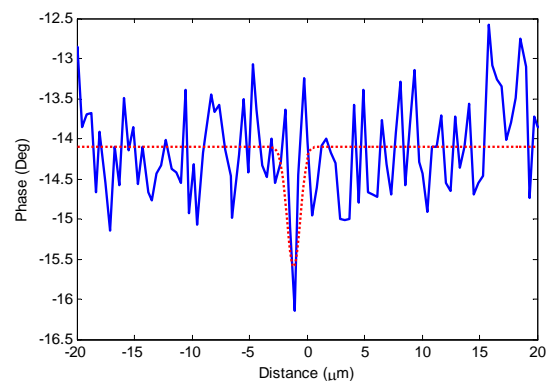
FIGURE 1. Thermal wave signal detected with a coaxial configuration of pump and probe beams in an oxidized NiCr alloy. (The solid line is experimental data. The dashed line is a guide to the eye.)

The third configuration allows us to clearly identify the grain boundary. In this case the pump beam is placed few spot sizes away from the location where the oxidized boundary is thought to be. The boundary interface is located at the origin and the pump is located 3.5 μm away (to the right in Figure 2) from the interface. The literature states that the phase lag between the thermal wave and source is typically a linear function of the distance for a homogeneous sample, as seen in the top pane of Figure 2. A kink in the phase is identifiable at the interface as shown in the top of Figure 2. Thermal wave, however, acquires additional phase lag as it propagates across an interface with large thermal resistance. This small perturbation to the phase profile is clearly identifiable if the linear background phase signal is removed (bottom pane in Figure 2). The linear background subtracted profile clearly demonstrates the additional offset introduced by the thermal resistance of the oxidized interface. Further evidence is obtained by measuring the thermal wave profile for different separation between pump and grain and verifying that the onset of the phase offset shifts accordingly.
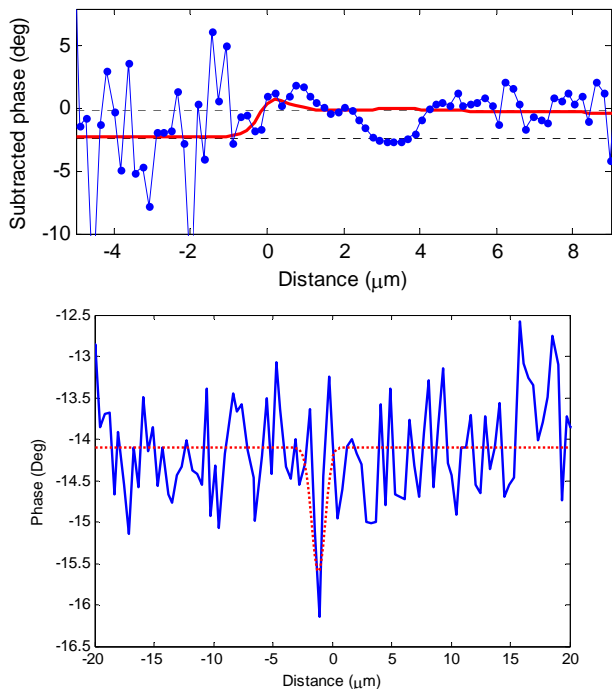
Experimental signals shown in the figures were acquired from pre-oxidized NiCr samples provided by Steve Bruemmer of Pacific Northwest National Laboratory. We applied these techniques to a variety of sample types: bulk Al, bulk Cr, bulk Ni, and oxidized Ni/Cr. Our original intention was to obtain high fidelity data using a femtosecond laser system. However, the lingering electronic response (due to ultrafast heating of the electron gas) overshadowed the thermal response. As a result, a simpler setup using a continuous wave (CW) laser was used. However, the CW-based system suffers from a lower signal-to-noise ratio due to poor laser stability. Despite this limitation, the CW-based system allowed us to demonstrate the feasibility of using laser-based thermal wave imaging to characterize oxidized grain boundaries. A higher quality laser system will yield higher fidelity data.

Benefits to DOE

The ability to perform in situ characterization of intergranular particle diffusion will provide insight into the mechanisms of stress corrosion cracking. Our results will provide valuable data to researchers who develop models to understand corrosion at the nanoscale level, which falls under the scope of DOE's Basic Energy Sciences office. This approach will also help position INL as a leader in the development of stress corrosion cracking mitigation strategies. The outcomes of this work will improve the understanding and prediction of long term environmental degradation of materials in nuclear power plants and materials in other harsh environments.

Relevant Publications and Presentations

S. Teysseyre, M. Khafizov, D. Hurley, and T. Lister, "Development of Laser Based Techniques for In Situ Detection of Environmentally Assisted Degradation of Materials," *The International BWR and PWR Materials Reliability Program Conference and Exhibition*, *July 16–19, 2012*.

FIGURE 2. A spatially resolved thermal wave profile across an oxidized grain boundary in an NiCr alloy sample. The blue dots are experimental data and red line is fit of experimental data with the thermal wave model.

Reactor Coolant Pump Alternate Can Material Development Program

Mark Carroll, Richard Wright, Ross Klein,[1] and Robert Ladefian[1]
12-112

A cooperative development program is underway to develop a tailored alloy system suitable for specific components in reactor coolant pumps (RCPs) produced by the lone U.S.-based manufacturer, Curtiss-Wright Flow Control Company. A considerable amount of RCP efficiency is being lost through parasitic electrical fields being developed in the powerful induction motors, and to address this issue a customized alloy system is being developed that will have a measurable effect on increasing RCP efficiency while meeting the considerable number of additional performance characteristics necessary in elevated temperature and controlled chemistry nuclear environments. Considering the extremely long service lives and the enormous power requirements of RCPs, a materials selection strategy that results in even fractional increases in pump efficiency would be a successful outcome of this development program. The combination of nuclear expertise and materials science and engineering capabilities of INL, along with the industrial and power plant production expertise of Curtiss-Wright, will engender a level of capability that is considerably elevated as opposed to addressing the specific issues alone by either party.

Summary

The initial efforts are largely the responsibility of INL, with a specific focus on the development of a tailored nickel-based alloy having increased electrical resistance properties that is further designed to retain a stable microstructure for long-service components. The capability to execute high-purity vacuum induction melting (VIM) of small alloy "buttons" (Figure 1) roughly 30 g in mass has been refined at the IRC in order to meet the rapid turnaround necessary to satisfy the comprehensive test matrix of customized Ni-Cr-based compositions, with elemental fractions selected through the generation of ThermoCalc-based phase field ternary models of the specific ranges of interest. The proven capabilities of Ni-based alloys in harsh or high-temperature systems makes them an ideal matrix material for further improvement through controlled elemental additions in order to engineer idealized properties. As a result of the initial casting trials and subsequent microstructural characterization, which included both energy-dispersive spectroscopy secondary phase identification and x-ray

diffraction for phase peak identification, a down-selection of candidate alloys has been carried out in order to scale up the more promising compositions. Based upon the compositions evaluated on small-scale heats, four castings more representative of full-scale production were produced at the end of FY 2012 by Sophisticated Alloys, Inc., with 50-lb billets presently being rolled into sheet and plate to more accurately reflect the hot-worked microstructure of the fabricated components. A direct microstructural comparison between button castings produced at INL (Figure 2) and industrially-cast experimental billets will provide validation for the pre-evaluation of candidate alloys through small-scale castings, while the full experimental analysis (to include mechanical and physical property evaluations) of the larger billets, both in as-cast and hot-rolled conditions, will provide the necessary bulk-property data to support the viability of the tailored alloys for deployment in the end-use components. Based upon the early evaluations of the tailored alloy microstructures and the establishment of relative compositional limits, a joint invention disclosure (IDR # BA-744) was filed for the initial alloy composition space under comprehensive analysis.
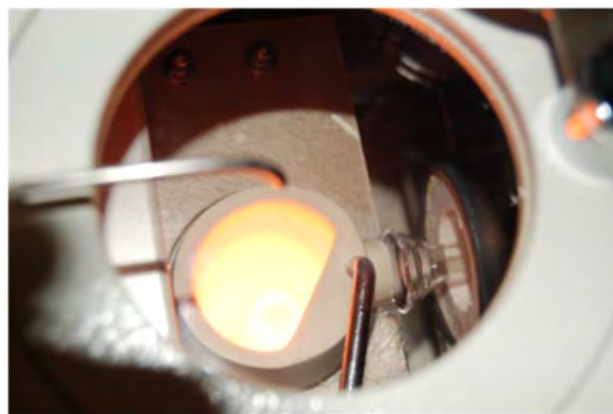
FIGURE 1. Vacuum-induction melting button-sized alloy compositions for rapid evaluation of properties.
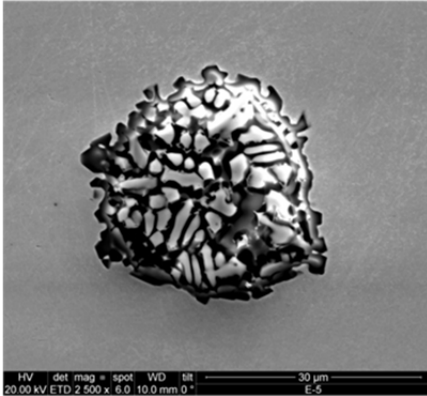
FIGURE 2. Analysis of secondary phases in VIM castings to evaluate impurity content.

The continuation of the project in FY 2013 is focused on mechanical and physical property testing of the industrially-processed alloy sheet as well as on continued evaluation of alternate alloy systems based upon the rapid alloy matrix casting protocol developed for the nickel-based alloys using VIM buttons. More detailed microstructural analysis on mechanical test specimens through appropriate electron microscopy techniques will also be an important contribution to the final alloy analysis and ultimate evaluation for use. Year two of the program is involving the industrial partner in an increased direct role, as the evaluation of tailored alloys expands to include extensive welding and fabrication trials of the most promising custom alloys.

Benefits to DOE

This developmental effort allows a U.S. national laboratory to directly interact with the nuclear industry by providing R&D technical solutions to measurable losses in plant efficiency, and help facilitate the continued leadership in nuclear-based technology by U.S.-based manufacturers. Increased plant efficiency will allow proven designs to continue to be utilized in modern plants, as well as to provide critical additional efficiency ratings to future small modular reactor (SMR) designs—all of which are envisioned to play important roles in energy generation that extend beyond the common need of supplying power to the electrical grid. Incremental improvements to the efficiency of reactor coolant pumps through tailored material systems will ensure that this type of design keeps U.S.-based manufacturing competitive in the growing international nuclear power sector.

Relevant Publications and Presentations

None.

Monitoring and Control of the Hybrid Laser-GMAW Process

Denis Clark, Dennis Kunerth, and Tim McJunkin

12-116

As part of the DOE-NE efforts to develop advanced reactor technologies, it is recognized that more efficient materials fabrication processes need to be developed and implemented. One such technology is the hybrid laser-gas metal-arc welding (GMAW) process to join metal components. The extra power input from the laser provides the production advantages of welds with less filler material and significantly higher travel speeds compared with GMAW only, and reduced weld preparation fit-up tolerances compared with laser welding alone. Properly applied, it also has the potential to reduce residual stresses and increase fatigue life. The dynamics of this relatively unknown process provide scope for the integration of advanced weld control models and nondestructive sensing technologies into the process to provide real-time diagnostics and control. The experimental approach is to use a number of sensing and diagnostic tools (ultrasonics to monitor subsurface weld pool geometry and defect formation, image processing to monitor temperature profiles and weld pool surface profiles, welding process electrical parameters, and various potential sensors for laser/weld pool interaction). The development of these experimental techniques may spin off useful sensors and algorithms for industrial applications, but the more interesting prospect is the idea of examining a process in an integrated way from fundamental phenomena to application specifics. Particularly as lasers become more powerful, versatile, and inexpensive—in parallel with sensor processing capabilities—an overall understanding of the process holds real promise for large productivity gains. (See Figure 1 for a visual summary of the process description.)
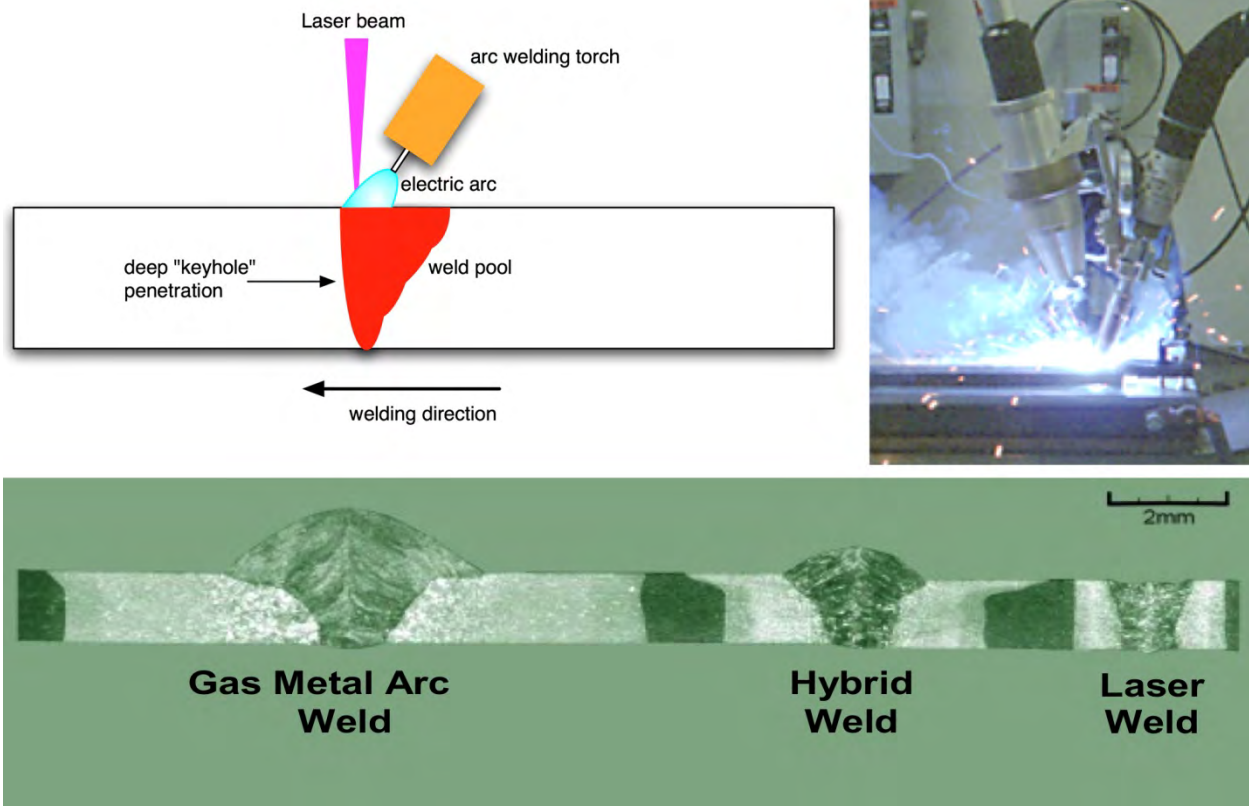
FIGURE 1. Visual summary of the Hybrid Laser-GMAW process.

Summary

This relatively small LDRD project was devoted, in its first year, to the activation of the existing GSI Lumonics AM-356 laser at INL's Research Center. This laser had been used at the manufacturer's laboratory in Detroit for a previous hybrid welding project on the high speed welding of ultra-high strength coated steels for automotive applications, in conjunction with the American Iron and Steel Institute. It was purchased by INL when GSI Lumonics downsized the Detroit facility. It is a 4 KW, continuous wave YAG ($Y_3Al_5O_{12}$) laser, delivered through a 600 µm fiber. This arrangement is quite suitable for the hybrid process, as the laser head can be positioned next to a Gas Metal Arc Welding torch at an appropriate angle. The process concept, the process in operation, and cross sections of laser hybrid welds are shown in the accompanying figure.

Benefits to DOE

A significant related opportunity occurred midway through the program year, with a call for proposals by DOE under the Nuclear Energy Enabling Technologies (NEET) program. Laser hybrid welding is an obvious "enabling technology" for its potential productivity and the desirable microstructural characteristics it can impart to welds in materials of interest in this industry. The LDRD led to a successful NEET proposal that was funded by DOE. The LDRD project was terminated in order to be compliant with the DOE Order. Much of the LDRD proposal background material was quite applicable to the proposal.

As evidenced by the successful proposal to a DOE-NE call, the LDRD work scope covered by this project is important to the energy and fabrication industries in general and the nuclear energy industry in particular.

Relevant Publications and Presentations

None.

Feasibility of a Broad Application Test Reactor Using LEU

Hans Gougar, Michael Pope, and John Ryskamp
12-117

This project explores the feasibility of using low enriched uranium (LEU) fuel to drive a materials test reactor to meet the irradiation needs of current and future ATR customers as the useful life of ATR comes to a close. Although the fuel and structural components of ATR can, presumably, be indefinitely replaced, the cost of doing so under an increasingly stringent regulatory regime may exceed that of a replacement facility. This was the motivation behind a previous INL project that yielded the conceptual designs of two possible replacements for ATR.

While this project is also looking at replacement designs, we had the additional constraint of operating on uranium enriched to no more than 20%. To achieve comparable performance (flux, cycle length, etc.), the LEU fuel must have a comparable fissile isotopic density. Under the Reduced Enrichment for Research and Test Reactors program, such high density fuels are under development and, for the purposes of this study, will be assumed to be available. The higher U-238 content, however, affects the fuel geometry and neutronics to the extent that the results and conclusions of the earlier Broad Application Test Reactor (BATR) analyses may no longer be valid. The first objective of this project is, therefore, to repeat the BATR neutronics analyses with both highly enriched uranium (HEU) and the proposed new LEU fuel (U10-Mo) to confirm acceptable performance and provide a baseline for evaluating the performance of any subsequent design variants.

Unlike ATR, a new test reactor may be required to accommodate a wide range of missions and customer requirements beyond fuel and material testing in pressurized coolant loops. Therefore, a second objective of this project is to identify the missions of high flux reactors in North America and gather the performance and operational requirements. The performance and operational requirements of these missions will be used to assess compatibility and to identify conflicts that would prevent dual or multiple use.

The conversion of ATR to LEU fuel is constrained by the needs and design of the existing facility. The design of a new test reactor is not as constrained. The flexibility to efficiently serve a broad array of irradiation needs as well as those of the naval reactor programs will require creativity and investment in such features with standard instrumented leads, in-core instrumentation, online test placement, and reconfigurable/replaceable core components. The first step, however, is to determine whether the basic neutronics of the core will support the different objectives. The third objective is to explore design features that would both mitigate the effects of using LEU and allow the facility to pursue missions other than the primary one of controlled chemistry loop irradiations.

Summary

Toward Objective 1—Two leading concepts from the BATR project were reexamined using the SERPENT code. In general, agreement was acceptable between current results and the original results from the 1990s. In some cases where agreement was not achieved between the current Serpent work and both the original DIF3D and Monte Carlo N-Particle calculations, an independent review of SERPENT models was used to verify the models.

The modular-hexagonal (M-H) design was found to have a large amount of excess reactivity by virtue of the beryllium primary reflector. However, the separation of the fuel from the test locations by said beryllium carries a significant penalty in fast flux in the test locations. For this reason, the M-H concept in its original form was dropped from consideration.

The multiple annular (M-A) core displayed much better performance with regard to fast flux in test locations and very high thermal flux was available outside the pressure boundary tubes (PBTs). The stainless steel PBTs, however, carry a significant reactivity penalty, which could be overcome by use of aluminum. The necessary ASME code case, however, is an open question for using aluminum for this application. Also, layout of the PBTs and accessing fuel assemblies and test trains is an open question in the M-A design.

Analysis performed using the SERPENT code largely confirmed those conducted in the earlier INL study. The performance of the core using LEU fuel was also found to be comparable to the HEU-fueled concepts.

Toward Objective 2—Potential uses and associated requirements of a high flux test reactor with the functionality currently served by a handful of reactors in the United States (ATR, High Flux Isotope Reactor [HFIR], University of Missouri Research Reactor Center) were explored. The needs of the primary customers (DOE

Offices of NE and the Naval Reactor Program) were gathered through a survey and group discussions in March 2012. Survey results were documented in the second of three technical reports issued during the year. Assuming that the primary mission was achieved with loops and high density fuel, isotope production was found to be possible for certain isotopes with online insertion and removal. Neutron scattering in a beam tube to support interrogation of nuclear fuels and materials is also a possibility, however, having more than one beam tube would severely limit reflector irradiation volume.

Toward Objective 3—Some variations on the two BATR concepts were explored and advantages and disadvantages were identified. With regard to magnitude of fast neutron flux, the cases with aluminum racks held an advantage due to the lack of additional moderation. However, as an effect of this lack of moderation, low effective cross-sections lead to lower reactivity configurations than those designs with large amounts of moderator surrounding the fuel.

Most of the secondary missions identified for this test reactor are better served by large volumes of high-thermal neutron flux regions. All variants investigated were equipped with large secondary reflector tanks surrounding the core. Placing these outside the pressure boundary provides easier access to these test locations because penetrating the pressure vessel is not required for these test locations. Nominally, these tanks are specified to contain D_2O, which provides the highest thermal neutron flux of any materials considered. However, because D_2O would require sealing with some means of handling the tritium produced, beryllium was also considered. Though the secondary tank of any of these variants could be made to accommodate most of the identified secondary missions, some of them have higher neutron flux than others.

The cost of high neutron flux in a region outside the pressure boundary is, naturally, rapid accumulation of neutron fluence on that pressure boundary. All of the reactor variants presented here would have to

accommodate this. It is likely that the vessels or PBTs would need to be designed for replacement after a certain number of years. Alternatively, for some of the variants, the pressure vessel could be moved away from fuel, which would lower the neutron flux on the vessel, but also lower the neutron flux outside of it. The feasibility of using aluminum rather than steel for a pressure vessel or PBT has a significant impact on the neutron flux levels in the secondary tank and, in some variants, reactivity of the core. The additional licensing cost of such a design choice should be evaluated in future work.

Benefits to DOE

This LDRD was undertaken to meet a strategic need of the INL. However, discussions in FY 2012 emphasized the importance of the topic to DOE. Toward the end of FY 2012, discussions were held among DOE-NE senior management about how to continue meeting the increasing demand for irradiation services given: (1) the national security imperative to reduce the inventory and use of highly enriched uranium in civilian facilities; and (2) the difficulty and expense of maintaining and repairing the aging high flux test reactors operated by the federal government. It has been suggested that HEU-to-LEU conversion of ATR and HFIR may not be the most cost-effective way to do this and that a new high flux test reactor may be required. It is also recognized that replacing both ATR and HFIR in the current fiscal climate will be difficult. Replacing one of them will be a challenge but less so. It is, therefore, reasonable to explore whether one new facility can serve the missions currently served by multiple reactors. This will require extensive evaluation and discussions among DOE and laboratory personnel to evaluate the attributes of the existing reactors and to define and compare their mission requirements. It will also require some understanding of the different features of test reactors that lend themselves to certain missions. The work performed on this LDRD project in FY 2012 specifically addresses each of those issues. The three technical reports generated during the course of the year were forwarded to the appropriate DOE-HQ personnel.

Relevant Publications and Presentations

Pope, M.A., H.D. Gougar, and J.M. Ryskamp, "Evaluation of Broad Application Test Reactor Concepts with Low Enriched Uranium Fuel," Idaho National Laboratory, INL/LTD-12-25788, August 2012.

Pope, M.A., H.D. Gougar, P.D. Bayless, and J.M. Ryskamp, "Evaluation of Multi-Mission Test Reactor Concepts," Idaho National Laboratory, INL/LTD-12-27125, September 2012.

Gougar, H.D. and M.A. Pope, "Requirements, Supporting Technologies, and Recommended Scoping Investigations for a New Test Reactor Fueled with Low-Enriched Uranium," Idaho National Laboratory, INL/LTD-12-27111, September 2012.

Nuclear Hybrid Energy Systems Reactor Subsystem Modeling and Infrastructure Development for Integrated Hardware Testing

Shannon Bragg-Sitton and Piyush Sabharwall
12-129

Nuclear hybrid energy systems (NHES) are important systems for the future of energy in the U.S for a variety of reasons. First, NHESs could play a primary role in achieving energy security. Second, they may provide reliable power availability even with increasing renewable energy penetration into the power grid. Third, they may allow utilities to repurpose excess electricity in times of low demand. Incorporating a fission-based power source in a multi-output system (electricity and process heat) can offer significant advantages over carbon-based production sources such as coal or natural gas, including reduction in atmospheric carbon emissions. In an integrated multi-output system, thermal energy from the nuclear reactor subsystem can be diverted to industrial applications in times of low electricity demand. High temperature, high quality heat from advanced reactor designs might be used for hydrogen production or synthetic fuel production (coal-to-liquid or natural gas-to-liquid processes). Low temperature heat from advanced reactor designs or the current and future fleet of Light Water Reactors (LWRs) might be applied to desalination processes or be stored for later use in low temperature ammonia or hydrocarbon-based thermal cycles. Although small modular reactors (SMRs) are the focus of the present study, the concepts can also be applied to the current fleet of LWRs. A nuclear generation system can additionally complement highly variable renewable power sources, such as wind or solar power stations, in a multi-input system layout to produce steady baseload power to meet demand from the grid.

In an effort to better understand the requirements for such a system and to help make NHESs a reality, this project had two primary objectives:

1. Develop a preliminary dynamic reactor kinetics and heat transfer model that will be incorporated in a broader system model under development by INL researchers to characterize integrated system performance and to provide a platform for control system development.

2. Formulate a strategic plan for infrastructure development and demonstration of nuclear hybrid energy systems that will be incorporated in the INL Ten-Year Site Plan.

The FY 2012 research is coupled with ongoing system modeling with other NHES INL LDRD. Development of a coupled simulation platform is dependent on both the development of a balance of plant simulation via another INL-supported LDRD and progress made in integrating a preliminary reactor subsystem simulation (Project 12-124).

Successful completion of the modeling/simulation task will allow initial computational demonstration of a tightly coupled NHES to identify key reactor subsystem requirements, enable identification of candidate reactor technologies for a hybrid system, and highlight key challenges to operation of the coupled system. This work will provide a baseline for later coupling of design-specific reactor models through industry collaboration.

The FY 2012 strategic plan for integrated testing of hybrid energy system components requires significant cross-laboratory collaboration. The plan establishes the framework for a hardware test facility that will allow for component testing, partially integrated system testing, and fully integrated system testing including interfacing with the electrical grid.

Summary

Reactor Subsystem Modeling—The INL research team is currently developing a dynamic simulation of an integrated hybrid energy system. A detailed simulation of proposed NHES architectures will allow initial computational demonstration of a tightly coupled NHES to identify key reactor subsystem requirements, identify candidate reactor technologies for a hybrid system, and identify key challenges to operation of the coupled system. This work will provide a baseline for later coupling of design-specific reactor models through industry collaboration. The modeling capability addressed in this report focuses on the reactor subsystem simulation.

Many computational tools and methods are available for modeling a nuclear reactor, power conversion systems, and associated process applications. One method is to develop a single program capable of modeling the entire system. Another is to combine two or more existing computer programs, each modeling a portion of the system for which it is validated, where the programs exchange information to compute the solution. The former method requires a lengthy development and verification and validation process. The latter method leverages industry standard software to reduce development and funding requirements.

Preliminary balance of plant system models have been developed by INL researchers and are currently being enhanced to assess integrated system performance given multiple sources (e.g., nuclear and wind) and multiple applications (i.e., electricity and process heat). Initial efforts to integrate a Fortran-based simulation of a SMR with the balance of plant model are being completed in FY 2012 under support of another INL LDRD project (12-124). This initial effort takes advantage of an existing SMR model developed at North Carolina State University to provide initial integrated system simulation for a relatively low cost. These efforts are reported in a separate project report. Balance of plant component and subsystem models are written in the Modelica language which interfaces with the Dymola software package to allow solution of the complex set of coupled equations. Licenses for Dymola and the associated tool sets were purchased in FY 2012 to support completion of the system simulation development.

As the system model is enhanced, there is significant interest in adopting an industry standard software package to model the reactor subsystem and other integrated system components. The RELAP5-3D$^{©}$ code is a nuclear industry standard and provides the necessary dynamic coupling technique to connect to other component and subsystem simulations. This approach will allow adoption of standard simulation platforms used by researchers outside the nuclear field, recognizing that nuclear hybrid energy systems represent truly cross-cutting system architectures that bring together researchers from a wide range of industries and experience.

Dynamic code coupling capability with RELAP5-3D has been developed and exercised for over a decade. INL report INL/EXT-12-25195, "Nuclear Hybrid Energy System Modeling: RELAPs Dynamic Coupling Capabilities," documents the key features of the RELAP5-3D code dynamic coupling, as well as RELAP5-3D code architecture, capabilities, and verification and validation. The baseline system model was not at a development point that a full RELAP5 model could be integrated in FY 2012. The alternate path of using the Fortran –

Modelica co-simulation platform as a baseline system simulation for architecture analysis and future enhancement was instead adopted while using the LDRD task to fully define the unique capabilities of RELAP5 and potential code coupling methodology software.

Strategic Planning—A strategic plan for NHES development was issued August 30, 2012: *Nuclear Hybrid Energy Systems, Capability Development Plan* (INL/LTD-12-26528). This plan provides the strategic goals for NHES development:

1. Develop innovative approaches and enabling technology for industry deployment, including process design and simulation models, life-cycle and economic analysis codes, dynamic process integration and control tools, and unit operations tailored for integrated systems operation.

2. Reduce deployment risks through analysis, component and sub-system testing, concept and code verification and validation, human-machine interface resolution, and operator training.

3. Provide regulators access to robust, independent analyses and information, as well as observable scale-up of integrated process and system demonstrations.

Additionally, the report provides a five-year plan that leverages the progress of the past three years and leads to an Energy Park Demonstration Plan for candidate Energy Park Architectures. In this manner, the INL Energy Systems Laboratory (ESL) Hybrid Energy Systems Testing (HYTEST) facility offers a test bed for initial non-nuclear hybrid system demonstration that will inform the plan for build-out of an Energy Park with a prototype SMR. The five-year plan coordinates the INL missions and directorates to make effective use of LDRD investments, as well as directed Nuclear Energy University Program (NEUP) and INEST CORE projects. In this manner, foundational academic work performed by the universities complements industrial interests in developing the energy infrastructure for the future.

Benefits to DOE

NHESs are important systems for the future of energy in the U.S. due to their potential contributions to both energy security and efficiency. This project helps lay the groundwork for such systems. Successful completion of the system modeling and infrastructure planning work will position INL as a leader in both SMR and hybrid energy system development and demonstration. This work will allow researchers to hone in on requirements for reactor design and operating parameters and will highlight key needs for system development and testing. The capability development plan provides a defined path forward for enhancement of existing INL capabilities and development of new unique capabilities through collaboration with national laboratory, university, and industry partners. Successful demonstration of a nuclear hybrid energy system through enactment of the development plan will expand nuclear energy relevance and potential by creating more cost effective electricity and heat energy and will enable greater efficiency of renewable energy deployment while providing grid stability without substantial grid-scale energy storage, each of which are key to efficient use of energy resources and accomplishment of national energy security.

Relevant Publications and Presentations

Pasamehmetoglu, K., S.E. Aumeier, R.D. Boardman, S.M. Bragg-Sitton, L.A. Braase, and J.D. Herzog, "Nuclear Hybrid Energy Systems, Capability Development Plan," INL/LTD-12-26528.

Mesina, G., P. Sabharwall, N. Anderson, H. Zhao and S.M. Bragg-Sitton, "Nuclear Hybrid Energy System Modeling: RELAP5 Dynamic Coupling Capabilities," INL/EXT-12-27195.

NATIONAL
AND HOMELAND SECURITY

Laser-Induced Breakdown Spectroscopy: Development and Application of In Situ Elemental Analysis for Process Streams in Spent Fuel Reprocessing Facilities

Jill Scott, Jeremy Hatch, Timothy McJunkin, Andrew Effenberger Jr., and Cynthia Hanson
07-052

Toward meeting the challenge of detecting and identifying nuclear and radiological materials, INL has developed laser-induced breakdown spectroscopy (LIBS) systems for rapid, real-time elemental analysis of actinides in molten salts for monitoring reprocessing of spent nuclear fuels. Detection and identification of actinides during reprocessing will enhance the safeguards of nuclear and radiological materials by making material accountability within fuel cycle facilities less intrusive and more transparent. In-process measurements also will result in better detection of illicit activities through recognition and monitoring of characteristic process signatures and observables, reducing the risks of proliferate activities.

This project has involved development and fabrication of LIBS systems for analyzing molten salts and mixtures of radioactive metals from dried solutions. While the molten salt and radioactive samples did not require sample preparation, which simplifies the analysis process, each of the sample types and/or their environment proved challenging for optimizing a LIBS system.

Summary

This research has provided INL with a plausible methodology (LIBS) for rapid, real-time elemental analysis of metals in molten salts for monitoring processes related to spent nuclear fuels. During the first year of this project, an experimental LIBS apparatus for molten salts was developed using equipment and facilities at the University of California, San Diego. LIBS experiments on molten salts containing Cr, Mn, Co, K, and Li were performed to investigate best methods for working with molten salts and establishing calibration curves. In the second year, components were integrated to produce bench scale mockups of a LIBS system at INL capable of operations within the radiation facility constraints at the INL's Central Facilities Area (CFA) and Materials and Fuels Complex. During FY 2012, two key LIBS systems were assembled for experimental operations: (1) a LIBS system for non-radiological molten salt samples, and (2) a portable LIBS systems with fiber optic laser and light collection for conducting LIBS analyses on radioactive samples (e.g., U and Pu).

The LIBS system for non-radiological molten salt samples was designed to operate within an atmospheric chamber that was capable of operating in vacuum or with a bath gas (e.g., argon). LiCl-KCl based electrorefining salts, typical for fuel reprocessing, with various concentrations of metals were placed in a crucible and mounted in a heater inside the chamber. All of the molten salt LIBS experiments were conducted under a dry, argon environment to reflect the environment of electrorefining furnaces. Experiments validated that LIBS system measurements can be made on metals within the molten salt, dry argon environment and that improvement in detection limits can be obtained by using dual-pulse LIBS. Additional experiments were performed at various temperatures and determined that lower temperature solid samples gave higher intensity signals than the corresponding molten salts.

The portable LIBS system with fiber optics was designed and installed in a radiological laboratory at the INL's CFA, shown in Figure 1, and addressed safety requirements for working with radioactive materials. This system successfully obtained LIBS spectra of radiological samples containing Pu and Am within a high background of other metal salts. The resulting spectra are quite complex and point to the need for higher resolution to improve the confidence of identifying each actinide. Higher resolution also will enable measurements of the isotope ratios.
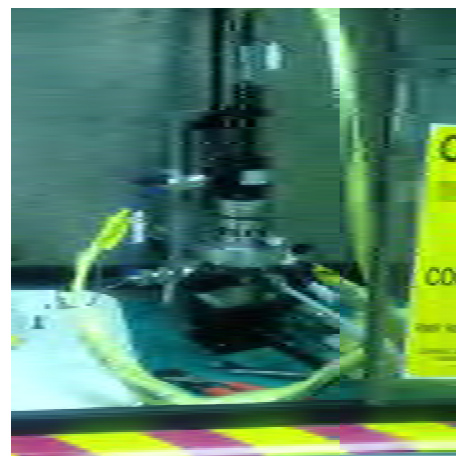
FIGURE 1. Compact LIBS system installed in radiological hood at INL's Central Facilities Area.

Benefits to DOE

Successful completion of this project advances DOE objectives to reduce the risk of nuclear material proliferation and provide technologies to improve nuclear safeguards. Improved monitoring of nuclear fuel electrorefining reprocessing will enable DOE and other interested parties (i.e., International Atomic Energy Agency) in handling and safeguarding nuclear fuels. In addition, these results will be useful to INL and DOE for developing more efficient actinide reprocessing methods under the Advanced Fuel Cycle Initiative and the Joint Fuel Cycle Study. During this LDRD project, two postdoctoral research associates and one graduate student (University of Idaho) were trained at INL related to LIBS and nuclear nonproliferation research.

Relevant Publications and Presentations

Scott, J.R. and J.J. Hatch, "Influence of Atmospheric Pressure and Composition on LIBS," in *Laser-induced Breakdown Spectroscopy (LIBS)*, New York: Springer Science, Chapter 4, 2012. (invited, in preparation)

Hatch, J.J., T.R. McJunkin, C. Hanson, and J.R. Scott, "Automated Interpretation of LIBS Spectra Using a Fuzzy Logic Inference Engine," *Applied Optics*, Vol. 51, B155–B164, 2012.

Effenberger Jr., A.J. and J.R. Scott, "Practical High-Resolution Detection Method for Laser-Induced Breakdown Spectroscopy (LIBS)," *Applied Optics,* Vol. 51, B165–B170, 2012.

Effenberger Jr., A.J. and J.R. Scott, "Effect of Atmosphere on Collinear Double Pulse Laser Induced Breakdown Spectroscopy," *Analytical Bioanalytical Chemistry*, Vol. 400, 3217–3227, 2011.

Effenberger Jr., A.J., J.R. Scott, and T.R. McJunkin, "Method and Apparatus for High Resolution Laser-induced Breakdown Spectroscopy (LIBS)," INL/BEA Docket No. BA-560. U.S. Patent Pending— Application 13/183,228 filed on July 14, 2011.

Scott, J.R., J.J. Hatch, A.J. Effenberger Jr., C. Hanson, and T.R. McJunkin, "High Resolution Laser-induced Breakdown Spectroscopy for Complex Spectra," *SCIX2012 presented by Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Kansas City, MO, September 30–October 5, 2012.*

Hanson, C., S. Phongikaroon, J.J. Hatch, and J.R. Scott, "Effects of Temperature Variation on LIBS Spectra of Molten Salt," *International Pyroprocessing Research Conference, Fontana, WI, August 26–30, 2012.*

Hatch, J.J., T.R. McJunkin, and J.R. Scott, "Comparison of Fabry-Perot Etalons for High Resolution LIBS Analysis," *ACS Northwest Regional Meeting, Boise, ID, June 24–27, 2012.*

Scott, J.R., B. Beardsley, G.S. Groenewold, S. Lammert, E. Lee, T.R. McJunkin, G. Ritchie, J.R. Almirall, and L. Becker, "Integrated Portable, Rugged Optical and Mass Instrument Suite (PROMIS) for Geologic, Biologic, and Organic Signature Characterization for Space Exploration," *Lunar and Planetary Institute and NASA Workshop on Concepts and Approaches for Mars Exploration, Houston, TX, June 12–14, 2012.*

Hatch, J.J., T.R. McJunkin, and J.R. Scott, "Recent Advances in Laser-induced Breakdown Spectroscopy," *Idaho Academy of Science, Idaho Falls, ID, March 22–24, 2012.*

Hatch, J.J., "Utilization of Spectroscopic Techniques for Surface Analysis," *Brigham Young University—Idaho, Rexburg, ID, October 27, 2012.* (invited)

Scott, J.R., "Technologies for Improved Sensitivity for Chemical Forensics," *FIU Department of Chemistry Seminar and IFRI Frontiers in Forensic Science Summer Seminar Series, Florida International University (FIU) and International Forensic Research Institute (IFRI), Miami, FL, July 27, 2011.* (invited)

Hatch, J.J., T.R. McJunkin, C. Hanson, and J.R. Scott, "Automated Interpretation of LIBS Spectra Using Fuzzy Logic Inference," *NASLIBS 2011, Clearwater, FL, July 18–20, 2011*.

Scott, J.R., A.J. Effenberger Jr., and T.R. McJunkin, "Economical High-Resolution Detection Method for Laser-Induced Breakdown Spectroscopy (LIBS)," *NASLIBS 2011, Clearwater, FL, July 18–20, 2011*.

Effenberger Jr., A.J. and S.G. Buckley, "Detection of Common and Trace Elements in Molten Salts Using LIBS," *NASLIBS 2007, New Orleans, LA, October 8–10, 2007*.

On-line Monitoring of Actinide Concentrations for Advanced Aqueous Separation Processes

Jan-Fong Jue, Shelly Li, Steven Herrmann, and Scott Herbst
09-068

Major obstacles to expansion of nuclear energy include proliferation concerns and control and accountability of nuclear materials such as actinides during spent fuel reprocessing. Monitoring actinide concentrations in the process streams is very challenging due to the highly corrosive and radioactive environment involved. Existing off-line sampling and analysis methods are both slow and expensive. To solve these problems, this project is developing an on-line, sensor-based technology for near-room-temperature actinide concentration monitoring.

Since the electrolyte materials for on-line electrochemical sensors are not currently available, identification and synthesis of new ionic conducting materials was completed in the first and second years of this project. After good quality sensor materials were successfully synthesized, sensor testing was evaluated in the last 9 months of this project.

Summary

The ideal actinide sensor materials for the aqueous separation processes should have high trivalent ionic conductivity near room temperature, good corrosion resistance in acidic aqueous solutions, good radiation damage resistance, and quick response to concentration changes in the solutions. After careful evaluation, NASICON structured oxides $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ were selected as the composition for a solid electrolyte due to its moderate trivalent ion conductivity and good stability in a high radiation environment. Dense and nearly single phase cerium conducting NASICON material was produced. The room temperature conductivity of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ measured by AC impedance spectroscopy met the conductivity requirements for the sensor applications ($>10^{-6}$ S-cm^{-1}). Computer simulation was also carried out in parallel on the selected Ce-NASICON structure. The possible cerium-conducting pathways in the reference Ce-NASICON were determined. This information is beneficial in explanation/prediction of the selectivity of Ce-NASICON in complex aqueous solutions.

Sensor performance testing began in FY 2011 and continued into FY 2012. Custom experiment setups were designed and manufactured. Extensive sensor testing in cerium-bearing aqueous solutions was performed. In general, the sensor response is not ideally Nernstian but there is a good linear response to the concentration difference. There is a change in the magnitude of the response when in the presence of strong acid but the response is still distinct. No adverse corrosion effects on a NASICON solid electrolyte were observed after testing in acidic aqueous solutions. The results obtained to date clearly prove the concept of using trivalent conducting NASICON for actinide sensor applications.

Benefits to DOE

This project resulted in the development of technology solutions that are applicable to DOE needs for a safe and proliferation-resistant fuel cycle in support of the U.S. nuclear industry and national energy strategy. Aqueous separation processes developed for treating spent nuclear fuels is a key component in this advanced fuel cycle. Successfully developing sensor-based actinide monitoring technology will provide a reliable and cost effective way to monitor as well as safeguard spent fuel treatment processing facilities.

Relevant Publications and Presentations

Boston University is preparing a manuscript for journal publication.

Jue, J-F., S.S. Li, T.P. O'Holleran, S.M. Frank, and B.F. Cowan, "Development of Ceramic Sensors for On-line Actinide Monitoring," *The 34th International Conference & Exposition on Advanced Ceramics & Composites (ICACC), Daytona Beach, FL, January 25–29, 2010.*

Jue, J-F., S. Herrmann, S. Herbst, S.S. Li, and S. Gopalan, "Development of Sensor Materials for On-line Process Monitoring," *The 35th International Conference & Exposition on Advanced Ceramics & Composites (ICACC), Daytona Beach, FL, January 23–28, 2011.*

Multi-Rate Shock Physics Simulation of Blast and Penetration Events in Concrete

Bill Richins, Tom Larson, James Blakeley, and Chris Pantelides[1]
10-064

Reinforced concrete is widely used in DOE/Nuclear Regulatory Commission/Department of Homeland Security-regulated projects to not only provide structural support but also mitigate the effects of radiation, possible malevolent attacks, and dynamic accidents. Even though concrete has been widely used for many decades, there is still much to be learned about its structural performance under varying environmental conditions. Nowhere is this more apparent than in construction needs for advanced nuclear reactors wherein reinforced concrete structural response to events including plant accidents and adversarial attacks is needed to fully assess the robustness of the designs. While computational modeling can and should help address concrete response to these types of events, concrete is a very complex material and behaves in complex manners depending on conditions such as curing time, age, aggregate composition, temperature, and rebar type. For example, observations of recent experiments at INL indicate that the dynamic strength of concrete increases at a slower rate than static strength during a typical 28-day curing process. To our knowledge, no material models capture this behavior. Current simulation methods employ a wide variety of concrete material models and parameters limited in application to specific strain rates making comparison of results between software packages difficult. The lack of dynamic test data also inhibits validation of modeling and simulation methods. As full scale testing of concrete structures is expensive or otherwise impossible to conduct, we hypothesize that the necessary concrete modeling information can be gained by conducting small-scale concrete sample testing and application of shock physics codes.

Summary

Initiated in FY 2010 the project identified concrete test sample designs that would likely be relatively straight forward to build and simulate. We issued a subcontract to the University of Utah (UU) to design and fabricate the concrete test samples and provide assistance with testing. Since the concrete form work and materials were donated by Hanson Structural Precast, we were able to significantly increase the extent of our planned testing. We supported two graduate students at the UU; Tim Garfield (2011 M.S. degree in Civil Engineering) and Annie Weidner (December 2012 M.S. degree in Civil Engineering).

We modeled benchmark problems to evaluate our ability to simulate dynamic concrete response to high explosive blast loading, impact loading (dynamic Brazilian test and dynamic uniaxial compression tests), and dynamic response at high temperatures. We conducted small-scale concrete testing to provide high quality data to compare, validate, and improve simulation results. Samples used standard steel rebar placement and three potential performance enhancing techniques: external fiber wrap, glass based rebar, and synthetic fibers.

In FY 2011, we completed blast testing of 19 concrete test panels 4 ft $\times$ 4 ft $\times$ (6", 10", and 14".) thick at the INL National Security Test Range. The reinforcement of the test panels varied in order to sample possible building material configurations. We used 10 to 20 lb of C4 explosive at a 1 m standoff from the center of the panel front face to ensure adequate damage without destroying the panels. Several panels were also strength tested at the UU to determine post-blast residual strength. Test results show significant reduction in concrete spalling and scabbing when using synthetic fibers in the mix or when the concrete test panels were retrofit with fiber wrap. Simulations (see Figure 1) of the response of the concrete panels to blast loading were undertaken using LS-DYNA (a multipurpose multi-physics simulation code commonly used at INL for dynamic impact simulations originally developed at Lawrence Livermore National Laboratory) and CTH (a shock physics code developed by Sandia National Laboratory).

An Impact Test Machine was built and installed at the UU to conduct the dynamic Brazilian split-cylinder tests. We conducted 44 such tests in July 2011 with INL providing test oversight, data acquisition, and high speed photography. In FY 2012, we conducted over 90 additional tests at high temperature (400°F) to provide vital data needed for advanced reactor designs. A Brazilian split-cylinder LS-DYNA simulation model was developed to compare with the dynamic experiments.

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[1] University of Utah
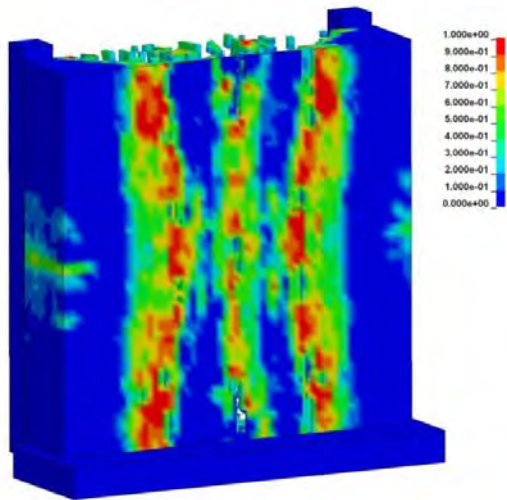
FIGURE 1. Front face of 25.4-cm (10-in.)-thick concrete panel subjected to blast load; (left) LS-DYNA simulation (1.0 = 100% damage); (right) test specimen results.

Several of these tests incorporated a glass fiber reinforced polymer (GFRP) wrapping material. Initially we planned to use a carbon fiber wrap. The use of carbon fiber to retrofit a large structure for blast protection is likely cost prohibitive for large structures. The following industry partners generously donated time and material for this project: Hanson Structural Precast – specimen construction and transportation, SikaUSA – GFRP laminates, Propex – synthetic fibers, and Hughes Brothers – GFRP bars.

Benefits to DOE

This project brings new analytical tools and capability to DOE, as well as a defined, peer-reviewed method to validate dynamic simulation of concrete structures in future safety analyses of nuclear or other safety-related systems. The exposure to difficult problems strongly enhances our nation's capability to perform future research and development in simulating dynamic events related to both nuclear power safety and national and homeland security. The LDRD developed analyses methods for evaluation of blast protection at critical U.S. DOE facilities is currently ongoing. The fiber wrap process is likely to prove a viable method to retrofit buildings, increasing blast resistance. The first complete set of dynamic tensile tests of high strength concrete at high temperature were completed along with companion dynamic and status compression tests. Results will soon

be published in both an INL external report and the Journal of Structural Engineering. INL, UU, and ATK Aerospace are pursuing a joint proposal to develop prototype acoustic emissions technology to evaluate the structural integrity of concrete connections as follow-on work to the research conducted during this project.

Relevant Publications and Presentations

Garfield, T.T., W.D. Richins, T.K. Larson, C.P. Pantelides, and J.E. Blakeley, "Performance of RC and FRC Wall Panels Reinforced with Mild Steel and GFRP Composites in Blast Events," *Procedia Engineering,* Vol. 10, 3543–3548.

Pantelides, C.P., T.T. Garfield, W.D. Richins, T.K. Larson, and J.E. Blakeley, "Behavior of Concrete Panels Reinforced with Synthetic Fibers, Mild Steel and GFRP Composites Subjected to Blasts," *Proceedings of the 2012 ACE Structures Congress, Chicago, IL, 23–34, March 29–31, 2012*.

Pantelides, C.P., T.T. Garfield, W.D. Richins, T.K. Larson, and J.E. Blakeley, "Performance-Based Evaluation of Concrete Wall Panels Subjected to Blast," *Journal of Structural Engineering*, ASCE, August 2012. (submitted)

Weidner, A.M., W.D. Richins, C.P. Pantelides, T.K. Larson, and J.E. Blakeley, "Drop Hammer Test of Concrete Cylinders Considering Fiber Reinforcement and Elevated Temperature," INL External Report, 2012. (draft in review)

Garfield, T.T., "Performance of Reinforced Concrete Panels During Blast Loading," MS Thesis, Department of Civil and Environmental Engineering, University of Utah, December 2011.

Weidner, A.M., "Dynamic Properties of Concrete and Fiber Reinforced Concrete at Room and Elevated Temperatures," MS Thesis, Department of Civil and Environmental Engineering, University of Utah, December 2012.

Garfield, T.T., W.D. Richins, T.K. Larson, C.P. Pantelides, and J.E. Blakeley, "Performance of RC and FRC Wall Panels Reinforced with Mild Steel and GFRP Composites in Blast Events," *ICM11-3709, 11th International Conference on the Mechanical Behavior of Materials, Milano, Italy, June 5-9, 2012.*

Pantelides, C.P., T.T. Garfield, W.D. Richins, T.K. Larson, and J.E. Blakeley, "Behavior of Concrete Panels Reinforced with Synthetic Fibers, Mild Steel and GFRP Composites Subjected to Blasts," *2012 ASCE Structures Congress, Chicago, IL, March 29-31, 2012.*

Next Generation Control System "Smart Grid" Simulation Environment

Lyle Roybal and Robert Jeffers
10-073

Long-term energy security has been identified as a high priority by Presidential directive and increased usage of renewable generation is emphasized to meet this need. Electric utilities are incorporating ever-increasing amounts of intermittent and distributed renewable electricity from wind and solar power generation. However, power generated by these sources can be highly variable and unpredictable. Wind and solar power have a random component in the short time-scale, a diurnal component in the mid-time scale, and seasonal component in the very long time-scale. In fact, renewable generators tend to display properties that are very similar to the system load profiles that a utility might encounter and are often classified as "negative" load by utilities. Therefore, the value of ancillary services such as frequency regulation and contingency reserves are greatly increased as utilities balance energy generation and load usage over multi-time scales, requiring the implementation of new load management strategies. To help develop such strategies, this project developed a method to model the aggregate effects of load management strategies and generation on the frequency stability of small- to medium-sized power systems over multiple time scales.

The Model for Electric Grid Strategies (MEGS) employs a hybrid modeling technique that can simulate the effects of complex load management strategies over multiple time scales using system dynamics and agent-based constructs to capture the complex dynamics of electric power systems. This technique can simulate the effects of new technologies such as electric vehicles that—when deployed en masse—may impact grid stability. MEGS can also simulate the contribution of individual consumer behavior to the operational needs of a power grid over multiple scales with sub-second resolution and is designed to simulate the behavior of frequency-responsive components such as intelligent load devices and generators.

MEGS is based on first-principal physics centered on the classic swing equation that converts rotational energy in generator shafts into electrical energy. MEGS is not a power flow solver, but a model to understand the frequency of tightly coupled power systems. It is designed to address problems associated with integrating intermittent generation by investigating the effects of individual generation control algorithms, system wide Automatic Generation Control (AGC) algorithms, and new load management control methods to balance load and generation profiles and ensure stable system frequency. MEGS simulates the most salient phenomena of power system physics including fine temporal resolution transients (100 ms) while providing multi-time scale modeling capability from a few minutes to several days to up to seasonal time spans for systems up to multi-gigawatt power levels.

Summary

The MEGS model was compared to and validated against data from an electric utility that experienced a slow generation failure, triggering a frequency deviation event that lasted several minutes. Approximately 140 MW of generation was gradually lost over a period of five minutes. Available system data included generation, load, and frequency as functions of time. A simplified MEGS simulation was created to validate the model by disabling or removing all the control algorithms for generation and load management initially developed for MEGS. The recorded data were used to calculate apparent total system inertia and then to "tune" the model to the specific physical system properties by matching the general characteristics of the frequency data. Figure 1 shows the results of the tuned model compared to the actual frequency recorded during this event.

MEGS can be used by power system analysts to design and analyze solutions pertinent to power system stability, but is focused on frequency and real power problems associated with distributed renewable generation and distributed load management practices. Because of its dynamic nature, the analyst can experiment with the latest in generation control and load management strategies including the ability to specifically implement real control algorithms and observe how they react to power imbalance events. On the generation side, individual generator control algorithms can be implemented, along with dispatch algorithms and system-wide AGC algorithms. Renewable power profiles can be imported from data files and modified with stochastic components

FIGURE 1. Frequency as a function of time for the simplified MEGS model compared to actual data.

as desired. On the load side, load profiles can be imported from data sets and "events" can be created to upset the power balance and observe how the modeled system responds. Because the loads can be divided into subsets, autonomous load-management controls can be postulated and created to observe how these virtual control systems respond to events and can be tuned to stabilize short-term frequency response until an appropriate generation adjustment can be made. These types of strategies not only make the system more stable, they also save money. Because MEGS uses a system dynamics implementation, operating costs can be implemented and system costs associated with control strategies can be calculated. This is a potentially huge benefit for utilities to optimize power generation under realistic dynamic conditions.

Benefits to DOE

MEGS benefits DOE by enabling the use of renewable energy while maintaining a more reliable and economical grid. The Department of Energy Office of Energy Efficiency and Renewable Energy (DOE-EERE) and the Office of Electricity, Delivery and Energy Reliability (DOE-OE) can both benefit from the development of MEGS.

Relevant Publications and Presentations

General Electric, Inc., "Model for Electric Grid Strategies (MEGS)," INL/MIS-12-26328, June 26, 2012.

INL Industrial Control Initiative Signature Briefing, "Model for Electric Grid Strategies (MEGS)," INL/MIS-12-26328, June 6, 2012.

Pacific Corp., "Multi-Time Scale Dynamic Modeling of Smart Grid Strategies and Solutions," INL/LTD-12-24392, January 11, 2012.

Peer-reviewed publications to IEEE (Institute of Electrical and Electronics Engineers) power journals are in process.

Wireless Communications R&D

Hussein Moradi, David Couch, Jose Loera, Behrouz Farhang,[1] Daryl Wasden,[1] and Arslan Majid[1]
10-075

Eliminating the need for fixed-frequency allocation for industry and government use is one of the key objectives of the U.S. Government National Broad Band Plan and the Office of Science and Technology Policy Wireless Communications Innovation Initiative. Many scenarios for spectrum sharing technologies have been identified by industry wireless operators and Public Safety first-responders to address their need for interoperability of various next generation wireless services.

To meet these needs, our LDRD project has developed a communication technology called Wireless Communications Spectrum (WSComm) that operates under the radio frequency noise floor to provide a secure, reliable, and sustainable Dynamic Spectrum Access link that maximizes efficient use of spectrum. This research has demonstrated that WSComm, when implemented across the Nation, is capable of eliminating significant spectrum allocation challenges, hence providing a foundation for spectrum sharing between industry communication carriers and government agencies.

Summary

Multi-Carrier Spread Spectrum (MC-SS) schemes such as Orthogonal Frequency Division Multiplexing (OFDM), (e.g., a modulation scheme employed in 4th Generation wireless communications systems), have been proposed as a robust technique to resist narrow-band and partial-band interference. WSComm, based on Filter Bank Multi-Carrier Spread Spectrum (FB-MC-SS) technology, enhances MC-SS and allows communications below the noise level. This breakthrough solves the fundamental limitation of cognitive/adaptive radio applications by providing a way to coordinate frequency assignments using a FB-MC-SS underlay control channel. WSComm is also adept in situations where Low Probability of Detection or Low Probability of Interception is needed and when there are requirements for low susceptibility to interference.

During FY 2010 we developed an initial concept design and improved upon the design using a mathematical model for FB-MC-SS. During FY 2011 and FY 2012, we constructed the initial WSComm prototype consisting of a transmitter, a receiver, and over-the-air RF front-end components with design objectives for a simultaneous "underlay communication channel" in an occupied spectrum delivering low to medium data-rates. The design objectives also addressed the following features:

- Resists high-energy narrow and/or wide band interference

- Exhibits low probability of detection and interception

- Performs robustly in high-speed mobility environment

- Poses no taxation on or interference to occupied spectrum

- Can be deployed on any band of frequencies

- Establishes a secure communications link when augmented with "key" generation feature

- When used as an "underlay control channel" creates a foundation to building an adaptive/cognitive radio network that maximizes the use of the available white spaces, where high-data-rate "overlay" channels are dynamically negotiated.

The WSComm was demonstrated to significantly improve throughput by reducing link errors, thereby providing a reliable and robust link operable in harsh environments, see Figure 1.
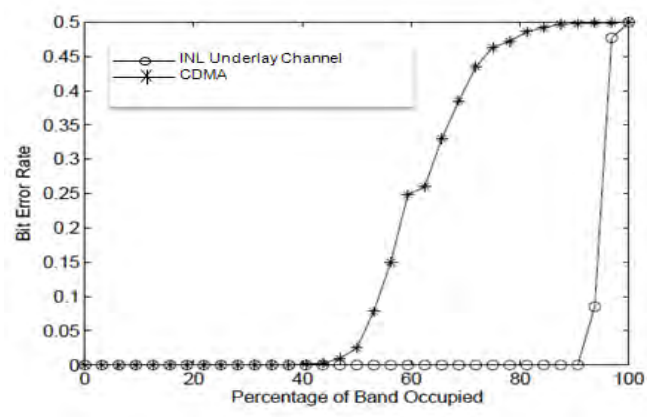
FIGURE 1. Improvement of Link Throughput using WSComm (shown as INL Underlay Channel). "Percentage of Band Occupied" is equivalent to interference. Zero Bit Error Rate is equivalent to an ideal communications link.

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[1] University of Utah

In FY 2012, this technology won R&D 100, Far West Federal Laboratory Consortium and Idaho Innovation awards. WSComm also earned the Best Demonstration award at the 2012 DySpan Conference, Institute of Electrical and Electronics Engineers leading international conference dedicated to advancing cutting-edge wireless technologies.

Benefits to DOE

The LDRD project advanced DOE's technical leadership in developing state-of-the-art solutions to address national challenges in spectrum availability as identified by the Office of Science and Technology Policy. Re-purposing and sharing of the spectrum benefits stakeholders in government, industrial spectrum license holders, and the users of unlicensed (ISM bands) spectrum. Also, as public safety transitions from P25 protocol to cellular based technology, WSComm offers a potential enhancement for secured push-to-talk, one-to-many communication capability.

Relevant Publications and Presentations

INL and UoU, "Design and Implementation of a Multicarrier Spread Spectrum Communication System," MILCOM 2012, Melbourne, FL, October 29–November 1, 2012.

INL and UoU, "Design and Implementation of an Underlay Control Channel for Cognitive Radios," *Journal on Selected Areas in Communications*, November 2012.

Patent Application Filing through TraskBritt PC Salt Lake City, Utah: US Patent Application Serial No. 13/331,357, Attorney Docket No. BA-585, "Methods and Apparatuses for Using Filter Banks for Multi-Carrier Spread Spectrum Analysis," December 5, 2011.

Moradi, H., "Spectrum Crisis Allocation, Autonomous Access and Device Security," MILCOM 2012, Melbourne, FL, October 29–November 1, 2012.

Electronic Warfare Digital Communications and Network Traffic Modeling

Kurt Welker, Tim Thompson, Lance Murri, Jerry Scott, and Kyle Schwieder
11-022

Being able to model network behavior is an essential capability in supporting critical infrastructure systems' efficiency, reliability, and resiliency. We are developing a software-based methodology to identify, extract, and assimilate communication network data and predict communication paths across networks and communications infrastructure. NetMuster—a proof-of-concept software prototype—provides the basis for mission planners, public safety responders, and infrastructure owners to understand and predict the reliability and resiliency of their communication networks (Figure 1). NetMuster uses both static (fixed equipment sites) and dynamic (mobile, real-time equipment sites) data sources; codifies the representative network systems; and provides an effects based mission planning, engineering level analysis (software modeling and simulation) of a network. Network data from various static and dynamic information databases (such as the Modernized Integrated Database [MIDB]), graphic data sources (such as ESRI© shape files) and real-time data feeds were assimilated into a common network representation. The methodology is sufficiently robust to resolve missing nodes and associations (i.e., the links between the nodes) and categorize components of the network. After a network is sufficiently defined using physics-based propagation models and system component performance specifications, this INL research capability can complete high fidelity engineering analyses on a communications network with radio frequency (RF) modeling and simulation. The NetMuster software was developed with novel capability for mission-planning-level (i.e., effects-based) traffic flow modeling that includes parametric representations of the domain infrastructure's "business rules" typically implemented by asset owner (i.e., NetMuster mathematically represents the comprehensive physical/cyber/business behavior and vulnerabilities of a complex hybrid communication network). The resulting graphical displays map the most likely pathway for network communications along with predicting alternative probable communication paths from one network component to another. When there is access to real-time network data, NetMuster can also resolve and display near-real time pathways for communications from mobile devices and platforms.

Summary

Over the course of this project we have created an overview of applicable information network sources for communications network data. This overview documented the data content and specified how that data could be utilized in a network traffic model. A proof-of-concept, working software prototype titled "NetMuster" was also designed and tested. The NetMuster concept, design, and software were externally reviewed by the USAF 453rd Electronic Warfare Squadron and the Air Force Research Laboratory.
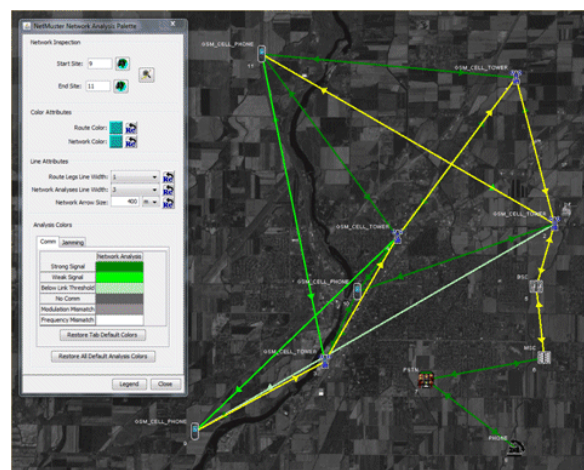
FIGURE 1. NetMuster Software Prototype for determining communications paths within a network.

The NetMuster software provides a mechanism for constructing networks that can then be modeled using physics-based engineering analysis to predict network behavior and vulnerabilities. Networks can be imported from geo-referenced shape files, from text-based flat files, or from a number of databases (such as MIDB). NetMuster implements a methodology and algorithms necessary to implement a logical-, physical- (reality-based or modeled) and effects-based, business-rule-driven network traffic flow analyses for: (1) logical only; and (2) multi-perspective that includes high fidelity physics-based signals propagation analysis. The NetMuster software implements algorithms that predict specific message routing within the network being modeled.

Benefits to DOE

The NetMuster capabilities support DOE objectives for securing the communication pathways integrated with the national electrical power grid and enabling the transmission of data necessary for implementation of the Smart Grid. NetMuster is intended to enhance the capabilities of the INL's National Wireless Test Bed to support future research, development, testing, and deployment of next generation spectrum sharing technologies aligned with the National Broadband Plan and Office of Science and Technology Policy's Wireless Innovation Initiative. This LDRD project demonstrated the potential impact of the integration of RF-propagation modeling, network, and communications pathway analyses, cyber security, and business response behaviors with future implementation of software defined radio or dynamic spectrum access technologies.

Relevant Publications and Presentations

Welker, K. and L. Murri, "Electronic Warfare Network Traffic Modeling," *Fiesta Crow '11 in San Antonio, TX April 13, 2011.*

Experimental Cyber Security Vulnerability Prediction, Discovery, and Mitigation

Miles McQueen, Jason Wright, Jason Larsen, Lawrence Wellman, Milos Manic,[1] and Dumidu Wijayasekara[1]
11-042

Even though the quantity and diversity of a control system's vulnerabilities are related to the system's security, there are few effective ways of predicting the density, discovery, reporting, and patch development of software vulnerabilities. Also, we don't fully understand how effectively vulnerabilities are being identified and mitigated. Consequently, we cannot easily determine or predict the degree to which a system is vulnerable to cyber attack. Critical infrastructure cyber security design, assessment, and measurement must take into account that software vulnerabilities exist in the system, and that the vulnerabilities require different levels of effort by an attacker to discover and exploit. Therefore, this research has initiated the development of controlled experimentation methods and observational studies to establish standards for vulnerability prediction, discovery, identification, and mitigation of software.

In conjunction with the goal of establishing standards for experiments in cyber security, we performed two significant investigations in 2011 with the potential to be of significant interest to the general cyber security community, and to produce experimentally verifiable predictions about future vulnerabilities which will aid situational awareness and anticipation of attacks. In 2012, resources were devoted to updating the initial work performed in 2011 with a particular emphasis on firm establishment of the misclassification of software bugs as "not vulnerabilities." In addition, we furthered the development of an automated bug classifier to aid software products development and maintenance teams in more accurate identification of those bugs likely to be vulnerabilities.

Summary

In late 2010, the vulnerability research organizations Rapid7, Google Security team, and Zero Day Initiative (ZDI) imposed grace periods for public disclosure of vulnerabilities. The grace periods ranged from 45 to 182 days, after which disclosure might occur with or without an effective mitigation from the affected software vendor. In 2011, we found no direct evidence that the shorter grace periods of 45 and 60 days were justifiable. However, there was evidence that the recently announced ZDI grace period of 182 days yielded some benefit in speeding up the patch creation process, and could be practical for many software products. In 2012, we updated the analyses and demonstrated that the early research results were holding and that vendors were now consistently meeting the 182 day grace period deadline (Figure 1).

We proposed two new vulnerability exposure metrics with the end-user in mind. Both metrics—Vulnerability Free Days and Average Active Vulnerabilities per day—depend not just on vulnerability lifespans of a product but also on the rate of vulnerability reporting. In 2011, we demonstrated the metrics in a case study using four browsers (Safari, Chrome, Firefox, and Internet Explorer). Based on the derived metric values for each browser, there were large differences in vulnerability exposure, with Safari having the lowest exposure (Figure 2). In 2012, we enhanced our case study through improved simulation and further demonstrated the earlier results. A paper was written and published about this effort.
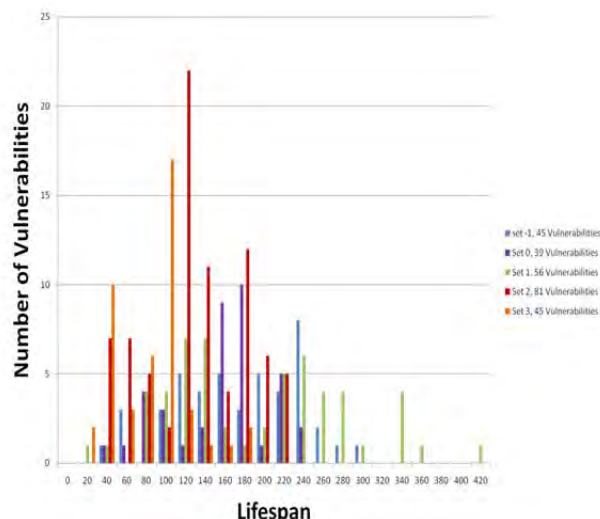
FIGURE 1. Vulnerability lifespans before 182-day grace period was imposed (Sets -1, 0, and 1) and after the grace period was imposed (Sets 2 and 3).
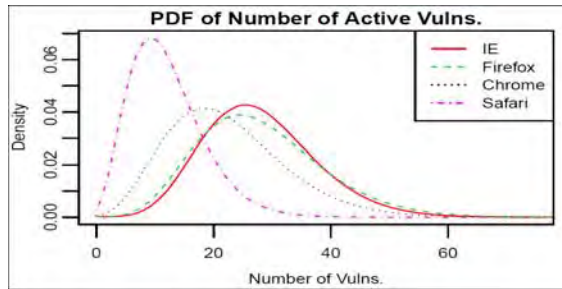
FIGURE 2. Average Active Vulnerabilities in four browsers.

In 2011, we initiated experiments into software vulnerability density, and conceptualized classifiers to more effectively and accurately identify those bugs more likely to be vulnerabilities. In 2012, we clearly demonstrated that for the experiment's chosen software product, the number of misclassified bugs is significant. With 95% confidence, we demonstrated that there is somewhere between 180 and 1,688 bugs (mean value of 523) which are also vulnerabilities but are not recognized

as such (Figure 3). This compares to a total of 107 known vulnerabilities for the given software product. Due to the significance of this result, many of the past decade's research results related to software vulnerabilities, and based on known vulnerabilities, are now called into question.

In 2012, we also progressed on the development of the automated bug classifier started in 2011 for identifying Hidden Impact Bugs. We have some very promising early results with the Artificial Neural Network (ANN) classifier providing a 69.73% true positive rate and a 2.5% false positive rate (Figure 4).

In 2011, we met with leading researchers and technical leaders to discuss their experiences and challenges in designing and executing credible cyber security experiments. The technical collaboration effort provided a research forum and aided development of a research community for improved scientific experimentation related to all aspects of the cyber security eco-system.

FIGURE 3. 95% confidence interval, per each score bin, for the number of bugs misclassified as not vulnerabilities in the chosen software product.

FIGURE 4. Confusion matrix for the ANN classifier. 69.73% true positives and 2.5% false positives.

Benefits to DOE

This research furthers the security of DOE information systems and achieves further recognition of DOE and its laboratories as technical leaders in cyber security research and development. The results of this project have established foundational science and experimental bases for cyber security vulnerability prediction, discovery, and mitigation that are notably absent in many current evaluations and technologies. Previously, cyber security evaluations and designs fell short in part due to a lack of a strong, experimental science basis of the underlying system security state and were often dependent upon personal experience, belief, and limited empirical evidence. With continued, scientifically based, improvement in our understanding, prediction, and identification of software vulnerabilities the risk management and the security of DOE networks and information systems as well as our Nation's critical infrastructure will be significantly enhanced.

Relevant Publications and Presentations

Wright, J.L., M. McQueen, and L. Wellman, "Analyses of Two End-User Software Vulnerability Exposure Metrics," *7th International Conference on Availability, Reliability and Security, Prague, Czech Republic, August 2012.*

Wijayasekara, D., J.L. Wright, M. Manic, and M. McQueen, "Mining Bug Databases for Unidentified Software Vulnerabilities," *5th International Conference on Human System Interaction, Perth, Australia, June 2012.*

Wijayasekara, D., M. Manic, and M. McQueen, "Early Identification of Hidden Impact Bugs: A Case Study," In Preparation.

Wright, J.L., J. Larsen, and M. McQueen, "The Misclassification of Bugs in Software Products: A Vast Increase in Estimated Number of Vulnerabilities." (in preparation)

These presentations are for 2012 only.

Presentation at Energy Security and Resilient Control Systems Workshop, Marina del Ray, CA, November 15, 2012.

2nd Annual Experimental Security Panoramas Workshop, Salt Lake City, Utah, August 14, 2012.

Conference paper presentation, Prague, Czech Republic, August 20, 2012.

Unconventional Radiation Detection Methods for Nuclear Nonproliferation, Safeguards, and Treaty Verification

David Chichester, Scott Watson, Edward Seabury, and James Johnson
11-059

Some of the technical challenges that are not currently met by today's nuclear instrumentation technology include wide-area, continuous radiation monitoring for safeguards monitoring inside centrifuge enrichment halls; wide-area radiation monitoring in higher throughput spent nuclear fuel handling and processing facilities; noncontact sensing methods capable of working within the high radiation fields of pyroprocessing hot cells; plutonium assay methods for advanced transuranic fuel forms; and high data rate signal processing for active interrogation of cargo and in stand-off screening systems. This project is exploring a set of innovative concepts aimed at advanced unconventional radiation detection methods to address these and other shortfalls. In some cases, these approaches are unconventional simply because they branch out beyond traditional sensor reliance on neutron and gamma rays. In other cases, they are unconventional because they seek to adapt measurement approaches developed in one field for use in a different way for very different applications.

Summary

Our goals for this fiscal year were to continue our exploratory research activities focused on examining the use of unconventional methods for detecting and measuring radiation for different nuclear security applications. In FY 2012 this work touched on several research areas. In early October the project supported a small exploratory subtask to study how low-technology, low-cost radiation detectors could be incorporated into a distributed sensor network for wide-area radiation field monitoring. This activity focused on the use of commercial-off-the-shelf (COTS) detector equipment and a COTS open-source, electronic prototyping platform.

This LDRD included an investigation into whether already-fielded equipment commonly used by law enforcement and military personnel could be adapted, with minimal cost, to function as radiation sensors for emergency applications. The project demonstrated this to be feasible and resulted in the submission of an INL invention disclosure record.

The major research thrust for this project this year has been to study the use of long-length scintillating fiber bundles for radiation detection. Custom developed instrumentation to support this task was acquired in the last quarter of FY 2011 and research studying the performance of this equipment took place in FY 2012. A research summary of our activity in this area has been accepted for presentation at the upcoming IEEE (Institute of Electrical and Electronics Engineers) Nuclear Science Symposium.

One of the highlights from this year's work was the design and development of a scintillating fiber radiation detector. Three long-length (~15 meter) scintillating-fiber bundles (SFBs) made using commercial BCF-10, BCF-12, and BCF-20 fibers (all from Saint-Gobain Crystlas, Hiram, Ohio) were designed and purchased. Each SFB was comprised of ten fibers (see Figure 1). The SFBs were engineered to efficiently couple into photomultiplier tubes (PMTs) through a custom-designed fitting. A 2-m SFB was also purchased for use in initial testing and small-scale trials. Experiments were performed to assess the relative performance of these detectors for radiation detection.
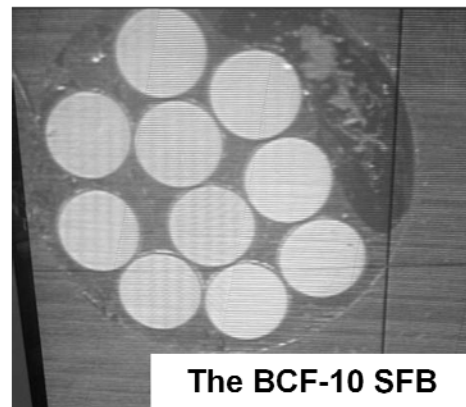
The BCF-10 SFB

FIGURE 1. A magnified photo of one end of the BFC-10 SFB, showing orientation and optical polish. Note the air gap in the upper right due to epoxy wicking up into the fiber bundle, this does not affect operation. For scale, note that the fibers are 1 mm in diameter.

The response of all three SFBs is exceptionally linear over a range of >15 m and they exhibit a spatial resolution of 0.5 to 0.6 m, depending upon fiber type and position along the fiber. Their efficiency was measured to be from 3.3 counts s^{-1} per mrem hr^{-1} to 26.9 counts s^{-1} per mrem hr^{-1} (0.33 counts s^{-1} per μSv hr^{-1} to 2.69 counts s^{-1} per μSv hr^{-1}) depending upon fiber type and location along the SFB. BCF-10 is the most efficient of the three fiber-types studied, while BCF-12 is the least efficient. With the best spatial resolution as well, BCF-10 appears to be the best candidate fiber, of the three studied, for use in sensor

arrays of length ~15m or less. However, with the longest 1/e length, the BCF-20 fiber type may be a better choice for longer length sensors. Further, the performance from a BCF-20 SFB could likely be improved by choosing a different PMT (photomultiplier tube) with a spectral response more closely matched to the longer-wavelength output spectrum of this fiber.

Further work is needed to improve the data acquisition electronics used for this work, in particular to lower the signal noise and improve the signal-to-noise relationships and allow lowering of the lower level discrimination in the trigger logic. Further work is also justified for studying, with improved data acquisition, the limits for how long a SFB is practical for these measurements. Lastly, it should be noted that the efficiency of the SFB-type sensors used here can be easily improved by including more fibers in the SFB assemblies.

Benefits to DOE

This research provides novel technical solutions applicable to DOE mission objectives for emergency response, nonproliferation arms control, and treaty verification. The continued improvement in capability to detect nuclear and radiological signatures with unique technologies enables the nation's confidence in the compliance of declared activities. Potential DOE programs that may be interested in this project include the National Nuclear Security Agency. In addition, an INL invention disclosure record developed as part of this project is under review for patent application.

Relevant Publications and Presentations

Chichester, D.L. and S.M. Watson, "Multispectral UV-Visual Imaging as a Tool for Locating and Assessing Ionizing Radiation in Air," *IEEE Transactions on Nuclear Science*, Vol. 58, 5, 2012.

SMC Advanced Armor Materials and Systems R&D and D&D

Henry Chu, Thomas Zagula, Michael Bakas, Benjamin Langhorst, and Jeffrey Lacy
11-060

This project is developing and testing novel materials for use as armor in the protection of military and security vehicles. These materials are designed for improved ballistic and blast survivability while requiring less weight to improve vehicle performance. Experimentation included the evaluation of new materials and characterization of their properties along with new synthesis and preparation methods that will be deployable as full-scale production processes.

In FY 2012, this project focused on four material technology objectives:

- Develop a heat treatment method for large scale bainitic steel samples and complete the characterization of mechanical properties to determine the suitability of the material as low-cost alternate armor steel.

- Verify and compare the effect of ferroelectric (FE) crystals on the reduction of penetration power of a shaped-charge (SC) jet with other conventional materials such as borosilicate glass, silicon carbide, and armor steels.

- Perform a preliminary study in using a self-propagating, high-temperature synthesis (SHS) process to create a super-hard titanium metal matrix laminate. The ultimate goal of this research program is to demonstrate that the SHS process is a viable technique in the fabrication of titanium laminate with dual hardness.

- Investigate the feasibility of using the spark plasma sintering (SPS) process to produce full-scale silicon carbide articles for armor applications.

Summary

Bainitic Steel. Based on the preliminary characterization results obtained in FY 2011, the chemical composition of bainitic steel, Type-N composition, was specifically designed by the INL researchers with the intent to develop an appropriate heat treatment process to optimize the strength, ductility, and hardness properties. Table 1 summarizes the properties achieved for an experimental $100 \times 100 \times 2.5$ cm prototype Type-N bainitic steel plate.

During FY 2013, heat-treated large scale bainitic steel samples will be ballistic tested at the INL National Security Test Range.

Ferroelectric (FE) crystal. Based on recommendations from U.S. Army technical reviewers, FE crystals were tested using 40-mm-diameter shaped-charge test devices. Three iterations of testing with the 40-mm SC devices (a total of 44 shots) were performed with three variants of FE to: (1) verify the behavior of the FE crystals with respect to standard armor materials such as armor steel, glass, and ceramics; and (2) characterize electrical discharge and/or electromagnetic field generated during the penetration by the SC jet and the breakdown of the FE materials. The comparison test of the FE crystals, armor-grade silicon carbide ceramic, borosilicate glass, and standard armor steel at maximum penetration-depth standoff were performed and the results are summarized in the plot shown in Figure 1. The comparison test revealed that the crystals (designated as T-X and T-Z in the plot) consistently offer better performance in terms of reduced depth-of-penetration, confirming the FY 2011 test results with 25-mm shaped-charge devices. Experimental measurements using a Pearson induction coil device have not been able to confirm the defeat mechanism hypothesis.

Dual hardness titanium. In FY 2012, multiple samples with a composition of 91 wt% titanium (Ti) and 9 wt% of amorphous boron (B) were fabricated using a newly designed steel pressing ram and die set for simultaneous initiation of the reaction and applied pressure. Experimentation to reduce the porosity in the end product determined that the effective application of pressure to attain the target porosity requires knowledge of the precise time of the formation of the soft to liquid phases in the material. A new pressing process is being considered and designed for FY 2013.

SPS of silicon carbide. A new research task began in FY 2012 to investigate the feasibility of fabricating large-scale silicon carbide articles using a developmental SPS process. Initial experimental results indicated that SPS is a viable method to manufacture large scale silicon carbide articles. The final density and hardness of the SPS SiC articles exceed those fabricated with the conventional pressureless sintering process.

TABLE 1. Properties achieved for an experimental 100 × 100 × 2.5 cm prototype Type-N bainitic steel plate.

[E]	0.2 % Yield	Strain@Yield	UTS	Break Strain	RA	Retained austenite	Hardness
(GPa)	(MPa)	(%)	(MPa)	(%)	(%)	V%	BHN
201	1,545	0.9549	2,042	4.74	4.64	16-25	600
(Msi)	(ksi)	(%)	(ksi)	(%)	(%)	V%	RC
29.2	224	0.9549	296	4.74	4.64	16-25	57
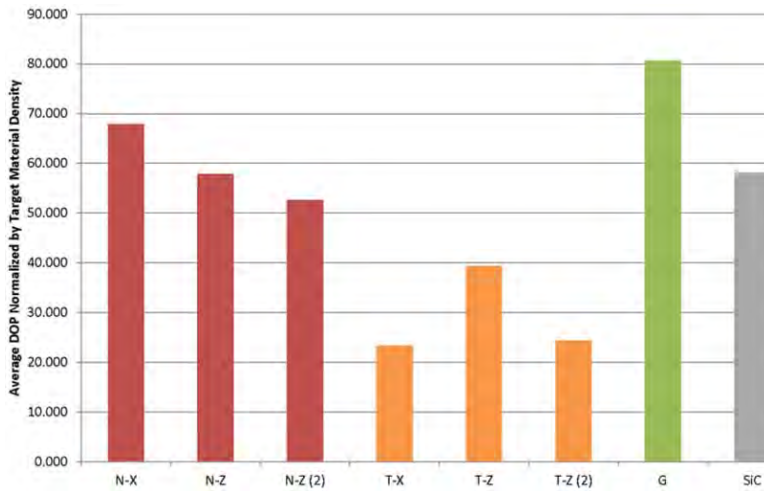
FIGURE 1. Comparison results of the FE crystals, armor-grade silicon carbide ceramic, borosilicate glass, and standard armor steel at maximum penetration-depth standoff.

Benefits to DOE

This project will enable future U.S. armor development and production in support of DOE/National Nuclear Security Administration, Department of Defense, and other customers. The materials developed in this program will be applied to robust protection systems to mitigate advanced threats for multiple vehicle platforms and applications.

Relevant Publications and Presentations

Due to the nature of this work, external release of this project's technical accomplishments have been limited.

Industrial Control System Threat Axis Analysis to Characterize and Quantify Malicious Intent from a Threat Actor

Peter Gasper, Daniel Noyes, Bri Rolston, Jason Wright, Robert Anderson, Rob Hoffman, Julio Rodriguez, and Lyle Roybal
11-069

The threat landscape for critical infrastructure systems is rapidly changing and poorly defined. Since there is a threat actor behind every threat, understanding and characterizing threat actors is critical to understanding the threat landscape. The Threat Axis Analysis technique being developed by this LDRD team consists of a technical knowledge base and a defined analysis methodology optimized to isolate, identify, and characterize threat actor capability and intent for critical infrastructure systems.

The technical knowledge base allows researchers to query information relating to the myriad of systems used in critical infrastructures. This makes it possible to define the technical thresholds that exist between traditional information technology (IT) systems and components and critical infrastructure systems and components. This is vital because threat actors use different tools, techniques, and procedures when targeting critical infrastructure systems versus traditional IT systems. By analyzing some of these key elements, the investigators have developed several research focus areas.

- *Network Threshold Analysis*: understanding the intent of a threat actor is a major component of understanding threat itself. Knowing if a threat actor is targeting a critical infrastructure system versus an enterprise system is essential to understanding a threat actor's intent. Our researchers have focused on defining network thresholds, which help analysts understand if a threat actor is targeting critical infrastructure systems.

- *Industrial Control Systems (ICS) Threat Terminology*: the term *threat* is often used but seldom defined. In the official Department of Defense dictionary, the term *threat* appears 150 times but is not a defined entry. Our research into this area attempts to define threat within the critical infrastructure systems realm.

- *Techniques for U.S. Adversary Capability Comparisons*: technical information from system intrusions often exists without attribution to the perpetrator of the intrusion. Because network engineers think and act differently from system engineers, it is possible to gain insight into who conducted certain intrusions by looking at how each intrusion is conceived and executed. Our researchers are building a process to analyze technical data in a way that builds a profile of the types of individuals and organizations that would be required to design and execute such intrusions, thereby homing in on the elusive problem of attribution.

- *Analysis of Technical Advances in Malware*: determining whether malware obfuscation techniques or reverse engineering techniques are advancing at the same rate is an important consideration with regard to threats to critical infrastructure systems. Our researchers are developing novel analyses to answer this question which will inform interested parties regarding the current state-of-the-art threat as it relates to malware obfuscation and reverse engineering techniques.

Summary

Information Search System. One new capability this LDRD has established at the INL is an optimized open source information acquisition network. This network was developed according to established requirements and is being used in an initial operating capability mode with foreign language machine translation software and lexical aids.

The INL's search system capability has been reviewed by a cognizant DOE open source liaison for robustness.

Product Review. LDRD team analysts have established a preliminary product knowledge base structure, cataloged data sources, and initiated data collection for knowledge base population. Data from critical infrastructure systems vendors were gathered and organized into a product knowledge base. The data emphasizes communication pathways to and from ICS components that perform critical infrastructure functions across all 18 U.S. critical infrastructures described by the Department of Homeland Security. This knowledge base will provide the INL with a unique capability to assist in securing critical infrastructure systems.

Benefits to DOE

This research furthers capabilities for threat information gathering and analysis for the protection of DOE/National Nuclear Security Administration, Department of Homeland Security, Department of Defense, other U.S. Government organizations and U.S. critical infrastructure. This LDRD will provide capability deployable for use by the Director of

National Intelligence Open Source Center as an option for information.

Relevant Publications and Presentations

"Threat Matrix," was presented at the DOE sponsored conference *Protecting the Nation's Power and*

Distribution System from Emerging Threats, November 2011.

"Threat Axis Analysis – Development of a Methodology to Characterize Threat Actor Capability and Intent – Interim Findings," was presented at the Naval Post Graduate School CATU, June 14, 2012.

Prototype INL Wildland Fire Early Warning and Situational Awareness System

Ryan Hruska, Kurt Derr, Matthew Anderson, and Mike Snyder
11-077

Early detection and efficient response are important in reducing threats and impacts from wildland fires. This research project successfully developed and implemented proof-of-principle prototype solutions for a future Wildland Fire Early Warning and Situational Awareness System. The project supported technical capabilities development to defend DOE infrastructure assets with fire suppression and emergency operations capabilities that reduce threats and damage from seasonal wildland fires. Our research was focused on: (1) the development of a prototype Wildland Fire Early Detection and Warning System; and (2) the development of prototype Wildland Fire Situational Awareness and Fire Behavior Model.

Summary

Much of the work for this project was completed in FY 2011. Funding was extended into FY 2012 to conduct experimental testing of the prototype INL wildland fire monitor and detection system and other government owned systems. The primary research focus was to determine if current technologies can improve fire department response times over the current method, which relies on human reporting.

Technical progress included:

- Completion of a camera placement analysis to ensure site coverage and minimize the number of cameras required to provide coverage across the INL range.

- Integration of a developmental, commercial smoke plume and fire detection software prototype with four INL cameras, configured to auto scan for sector-based monitoring. The system has demonstrated success in detecting smoke plumes for fires.

- Established capability to monitor the INL site for lightning strike location, through the automatic retrieval of lightning strike information from National Oceanic and Atmospheric Administration (NOAA) and visualize it within the prototype fire and plume detection software. This capability was licensed by the INL to a commercial vendor.

- Evaluation, selection and implementation of the U.S. Forest Service's Fire Area Simulator (FARSITE) for fire propagation modeling for the INL Emergency Operations Center.

Benefits to DOE

This project has benefitted DOE by providing emergency response capabilities to reduce threats and impacts from wildland fires. INL researchers and emergency responders advanced the scientific understanding of how a sensor system can be configured for early detection and how fire propagation models could be effective in planning fire suppression activities. This work will serve wildland fire researchers as well as helping to secure DOE facilities and resources.

Relevant Publications and Presentations

None.

Enabling Dynamic Spectrum Access in Long Term Evolution Networks

Juan Deaton
11-078

INL is developing network architectures and representative mathematical models to address the introduction of Dynamic Spectrum Access (DSA) technologies for mobile wireless broadband. Deployment of DSA technologies are proposed to address the demand for data arising from smart phone devices and applications within the next decade. This deployment of a DSA overlay in Long Term Evolution-Advanced (LTE+) networks will alleviate the projected 300 MHz spectrum deficit that the Federal Communications Commission predicts for mobile wireless broadband by 2014.

Summary

This project made two significant contributions into DSA research. The first contribution analyzed the operational effects of deploying DSA in a LTE+ Heterogeneous Network (HetNet), where both macro-cells and femto-cells serve the user population. This effort defined new protocol interfaces and the operational signaling required to deploy and manage DSA spectrum in a HetNet, which will serve as direct input to standards bodies for implementing DSA into next generation LTE networks.

Our second contribution was the development of a mathematical framework for optimally allocating spectrum in a macro-cell and heterogeneous network. Through the use of this optimization model, we compare the benefits of using opportunistic spectrum and the use of HetNets for increasing system capacity. To demonstrate the usefulness of this model, we created a realistic input network topology based on Global Information System data from population information, building foot prints, and cell tower sites. Using our realistic network topology, allocated frequency bands for cellular network traffic, and opportunistic spectrum (i.e., unoccupied TV and cellular channels), we were able to show quantifiable benefits between additional opportunistic spectrum and the addition of in-building femto-cell deployments to augment macro-cell coverage (i.e., HetNet). A rendering of our input topology and our results is shown in Figure 1. Results from this effort may provide input to the Federal Communications Commission for developing appropriate DSA regulation, which will allow for additional wireless services to emerge.
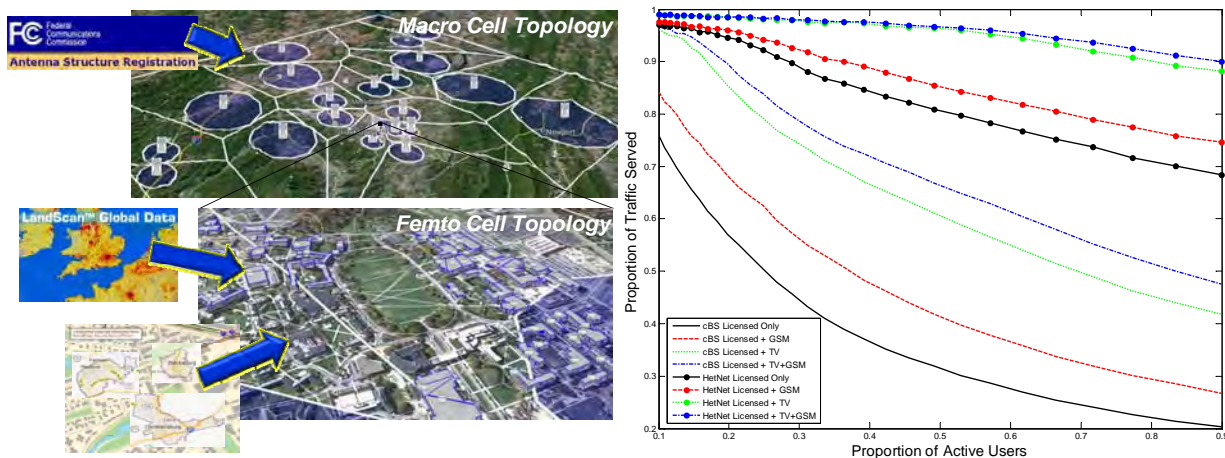
FIGURE 1. A rendering of our HetNet topology for our evaluations with macro-cell (i.e., cBS) topology (top-left) and femto-cell topology (bottom-left). Results (on right) show proportion of traffic served with increasing proportion of active users using only a cBS (i.e., macro-cell) and HetNet, without and with opportunistic spectrum (i.e., TV and GSM).

Benefits to DOE

Deployment of spectrum-sharing technologies will enable the efficient implementation of smart grid applications, which will benefit DOE. Future wireless networks will play a role in modernizing the electric grid and reliability of energy infrastructure. Additionally, the developed models will enable commercial networks and device uses within public safety and the military.

Relevant Publications and Presentations

Deaton, J., R. Irwin, L.A. DaSilva, and M. Benonis, "Supporting Dynamic Spectrum Access in Heterogeneous LTE+ Networks," *IEEE 7th International Symposium on New Frontiers in Dynamic Spectrum Access Networks (DySPAN), October 2012.*

Deaton, J., R. Irwin, and L.A. DaSilva, "Dynamic Spectrum Access in LTE-Advanced Networks," Elsevier Physical Communications: Special Issue on Cognitive Radio for LTE Advanced & Beyond (PHYCOM), November 2011.

Deaton, J., C. Wernz, and L.A. DaSilva, "Decision Analysis of Dynamic Spectrum Access Rules," *IEEE Conference on Global Communication (GLOBECOM), December 2011.*

Long Term Evolution Wireless Cyber Security

Kurt Derr and Corey Thuen

12-001

Long Term Evolution (LTE) is the new 4th generation mobile telecommunications technology that is based on the Internet Protocol (IP). LTE is opening cellular communications to new vulnerabilities and opportunities for malicious cyber attacks. In the next few years LTE technology will become pervasive in industry, government, and intelligently controlled infrastructure, as LTE offers a high-speed, high-bandwidth telecommunication option that enables new human-to-machine and machine-to-machine (M2M) applications. As development of LTE-compatible mobile devices moves forward, more software vulnerabilities will be discovered and impact asset owners and end users.

The objective of this project was to investigate, analyze, and test new 4G LTE devices to determine the degree to which cyber security vulnerabilities of 3G systems are resolved by new 4G protocols.

Summary

INL conducted vulnerability research of an Android smart phone that supports both 4G and legacy communications protocols with the long-term intent to identify and mitigate vulnerabilities in M2M applications used in LTE communication devices and their applications within critical infrastructure. The two phases to this vulnerability discovery research were: (1) initial testing of the mobile phone devices; and (2) testing LTE phones with a 4G communications system. Work this year focused on testing on the mobile phone device side while demonstrating a prototype 4G communications system at INL to enable future research testing with 4G. The device side testing used a vulnerability discovery methodology consisting of white box, black box, and gray box testing. White box testing using source code analysis resulted in the discovery of thousands of potential vulnerabilities. These vulnerabilities were correlated to published vulnerabilities from U.S. Computer Emergency Readiness Team and the National Vulnerability Database, to identify targeted vulnerabilities. This analysis determined that an overwhelming majority of the vulnerabilities will be false positives or unexploitable. Examples of the source code vulnerabilities found and categorized are shown in the following figure. The source code analysis has shown that the majority of potential vulnerabilities are with fixed sized buffers allocated by C code that represent opportunities for buffer overflows (Figure 1).

The black box testing involved the development of test cases for protocol fuzzing, during which a monitoring system was installed to monitor the output of the protocol fuzzing. Gray box testing involved reverse engineering the baseband processor. The objective was to identify the structure and flow of the code and to determine if there are any exploitable vulnerabilities in the baseband processor.
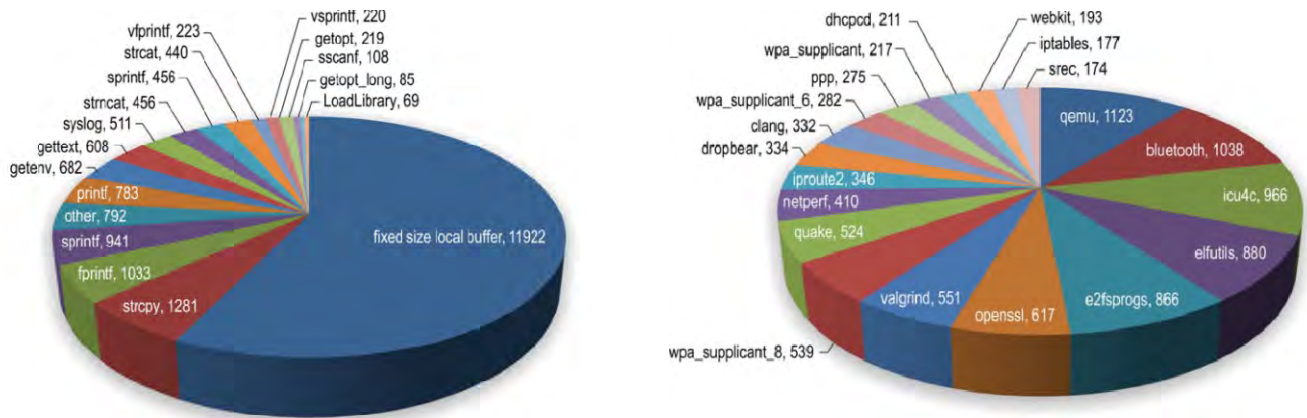
FIGURE 1. Source code analysis by C function and category.

Benefit to DOE

Understanding the vulnerabilities and countermeasures of mobile technologies and emerging telecommunications techniques such as LTE are important to enabling the operations of DOE, the Department of Homeland Security, the Department of Defense and, in general, U.S. public and private sector stakeholders around the world. The evolving introduction of more powerful and secure wireless communication devices will enable information assurance and the effectiveness, efficiency, and resiliency of U.S. infrastructure.

Relevant Publications and Presentations

None.

Polymer Components in Laminate Armor Systems for Ballistic Protection

Benjamin Langhorst and Henry Chu

12-017

The development of experimental methods that will enable improved use of polymers within new composite armor designs and resulting theories will lead to the deployment of armor solutions for future personnel, vehicle, and facility protection. Polymers have immense potential as materials in armor systems, but use has been limited by a lack of understanding of polymer armor mechanics and the optimal methods for their deployment. Currently, many theories exist regarding the penetration resistance of polymers and polymer laminates and these theories encompass a variety of polymer materials, configurations and ballistic threats.

To protect heavy vehicles, laminate armor systems have traditionally been used, but the introduction of polymers to the laminate systems requires an improved understanding of the effects of different design variables on armor performance. Woven personnel armor demands ultra-high performance polymer fibers to enable lightweight designs. The commercialization of ultra-high performance fibers has been limited by their susceptibility to environmental degradation, and INL devised a novel coating technology to enhance environmental stability. The proprietary coating could be applied to existing commercial fiber technologies that have known environmental susceptibility to enable their commercialization. INL researchers are developing these processes and experimental methods to enable the efficient use of polymers within new composite armor designs.

Summary

We have developed and demonstrated a novel ballistic test method that enables researchers to conduct comparative ballistic testing at less than half of the cost of traditional testing methods. To compare the performance of two slightly different armor materials or systems, projectiles are launched at targets in a traditional manner, but at velocities high enough to completely perforate the target. The residual projectile is captured in a "soft-catch" system, and its mass is measured. Figure 1 shows some of the residual projectiles that were captured after perforating targets. We demonstrated this method in FY 2012 and compared it to traditional methods of comparative ballistic testing. The novel method was found to require fewer than half the test events (resulting in a 50% cost and time savings) that the traditional method

required and the novel method provides statistical confidence levels to accompany the comparison.

FIGURE 1. Residual projectiles that were captured after perforating targets.

We conducted additional ballistic testing in FY 2012 to quantify the thermal environment to which polymer components are subjected during and after ballistic impact. Understanding the thermal operating conditions of polymer components in armor is important to assure that an impact does not cause large-scale melting. Laminate targets, featuring steel front and back layers sandwiching a polymer layer, were observed to undergo a near-instantaneous temperature rise as the shock wave from ballistic impact propagated through the target (Figure 2). The magnitude of the temperature rise depended on the velocity of the incoming projectile and the target design, but it was typically on the order of 10°C. The rapid temperature rise was followed by an exponential decay as the heat diffused to equilibrium. This data can be used to predict the thermal operating conditions of future polymer armor designs.

FIGURE 2. A polymer layer with embedded thermocouples to measure temperature during ballistic impact.

In an effort to enable the commercialization of ultra-high performance polymer fibers for lightweight woven armor systems, a novel coating technology was devised at INL and applied to a commercial polymer fiber. Commercial polybenzobisoxazole fiber is known to have rapidly degrading mechanical properties in the presence of high temperature and high humidity. INL researchers applied a proprietary treatment to some of the fibers while leaving other fibers in their raw, "uncoated," form. Fibers were subjected to environmental conditions and after a 28-day exposure, the coated fibers were observed to have significant performance improvement (Figure 3).
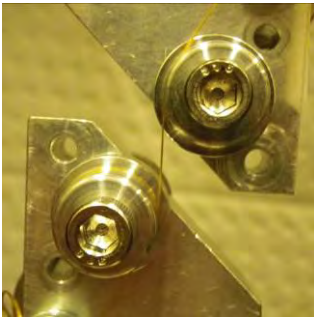
FIGURE 3. A coated PBO fiber undergoing tensile testing.

Benefits to DOE

The research included in this project will enable the rapid development of optimized armor to meet future protection needs of DOE/National Nuclear Security Administration, Department of Defense, and other U.S. Government entities. Improved armor leads to improved safety for U.S. soldiers and our allies and ultimately to a more secure nation.

Relevant Publications and Presentations

A paper has been drafted that presents a novel way to conduct comparative ballistic testing at less than half the cost of traditional comparative methods. The paper will be submitted to Experimental Mechanics.

Two abstracts have been accepted for presentation at the International Ballistics Symposium (Freiburg, Germany) in April 2013:

- "Novel Ballistic Testing Method to Compare Armor Materials or Components"

- "Impact-Induced Temperature Rise in Polymer-Steel Laminate Armor Targets."

Coupled Neutral to Charged Particle Transport Algorithms and Detectors

David Gerts, Richard Metcalf, and Ryan Clement
12-049

High energy photons are well described in most interactions using the neutral-particle Boltzmann Transport Equation (BTE). In general, however, the BTE cannot be inverted to solve the inverse problem for neutral particles from an unknown source. Specifically, the BTE has a solution set that is many-to-one for the forward problem (a specific detector response given a known source). When inverted, the BTE results in a one-to-many solution space. In general and from a rigorous mathematical perspective, this means that inverse spectroscopy cannot truly be solved. INL has experimented with a proposed approach by which the solution space can be significantly bounded, and probable solutions quantified based on the physical constraints of gamma-ray emission and transport. Physically, approximately 88,000 gamma rays are known to exist and, of these, only a few hundred are of realistic interest. Thus, although mathematically "any" solution is possible, there is a limited subset of solutions that are realistically feasible and of interest.

In addition to this limited quantity of probable gamma-ray emission lines, the physical interaction of high-energy photons also severely constrains the solution space. For high-energy photons, forward scatter is the most probable event, with minimal energy loss. However, significant energy loss can be obtained through large scattering angles. When a photon loses enough energy, it will be almost immediately absorbed into the environment. Therefore, high energy photons that reach a detector (of any sort) have either suffered no interactions or relatively few scatters at energies up to a few MeV. Therefore, an imaging approach based on probabilistic methods that takes into account physical realities can offer significant insight into unknown sources in the environment.

Summary

INL investigated hypotheses, detector concepts, and innovative algorithm solutions for coupled neutral to charged particle transport for inverse spectroscopy in support of future nuclear nonproliferation detection applications. This research emphasized developing the foundational principles for new inverse-spectroscopy algorithms and detectors designed to take advantage of these algorithms. First, derivation of fundamental transport theory of coupled neutral to charged particle inverse spectroscopy allows for this new approach. Second, conceptual detector design is modeled to utilize the inverse-spectroscopy algorithm. Although there is evidence of detector concepts potentially plausible for this work, these detectors have not been designed or optimized for nuclear nonproliferation applications.

INL investigated several detectors, including a new detector, based on silicon strip detectors. Silicon strip detectors are widely used in nuclear physics applications from synchrotron radiation to the Large Hadron Collider at CERN (European Organization for Nuclear Research).

Figure 1 and Figure 2 show two related concepts.
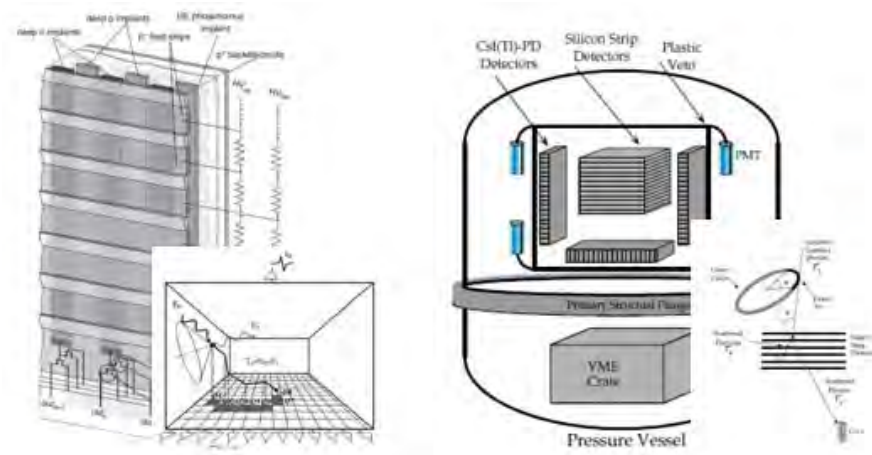
FIGURE 1. Detectors: multi-linear silicon drift detector (left), TIGRE telescope (right).
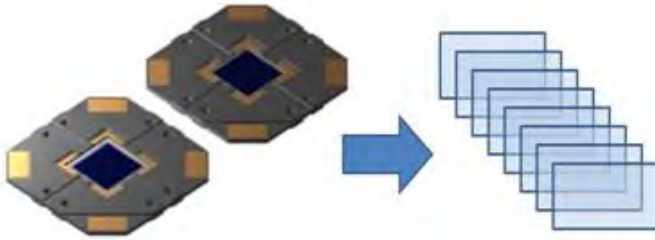
FIGURE 2. Concept drawing of multi-layer silicon strip detector (using Micron Semiconductor MSPSD DL-041 stackable strips).

Initial development of algorithms for handling the expected data, as well as the evidential theory for including new evidence addressed:

- Photon Physics
- Photoelectric Interactions
- Compton Scatter
- Gamma Conversion (Pair Production)
- Streaming Assumption
- Evidential Theory
- Conjunctive and Disjunctive Rules of Combination
- Automatic Multi-Dimensional Mesh Refinement.

A silicon-based array was designed for performance modeling against the conceptual algorithms.

Benefits to DOE

If successful this project will achieve changes in the capabilities of radiation detection in the field and in nuclear facilities in support of DOE and National Nuclear Security Administration nonproliferation applications. Such changes will help DOE meet its energy missions and national security.

Relevant Publications and Presentations

None.

Cross Section Representations for Nuclear Nonproliferation

Ryan Clement, David Gerts, and Scott Brown
12-050

INL is developing tools to evaluate and enhance the theoretical and experimental nuclear cross-section data available for nuclear simulation codes. As the nation's premier nuclear energy laboratory, INL maintains capabilities to accurately model nuclear fuel performance and behavior. A cornerstone of this simulation ability is the availability of accurate and up-to-date nuclear data.

Summary

This project's early work in reviewing several key nuclear decay quantities resulted in submission and acceptance of four errata and an additional accepted submission to a peer-reviewed nuclear engineering journal using the improved data. The research then changed focus from NJOY/ACE file representation to mobile nuclear data representation. The purpose of this change was to assist nuclear researchers in transitioning from printed materials to ubiquitous and freely available modern electronic distribution platforms. This work created two mobile applications: one for Apple's iOS and the other for Google's Android mobile device operating system. These two mobile applications are based on the National Nuclear Data Center's (NNDC) "Nuclear Wallet Cards." This work was performed in collaboration with Dr. Jagdish Tuli of NNDC.

The iOS work has lead to a peer-reviewed iPhone/iPad application on Apple's App Store and iTunes. NNDC has discussed the iPhone application at the recent nuclear physics/data community meeting at Argonne National Laboratory. The application is on the NNDC web page at http://www.nndc.bnl.gov/wallet/ (Figure 1).
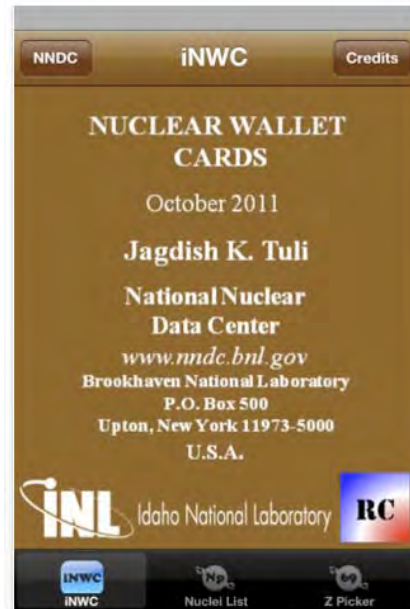
FIGURE 1. iNWC screen shot from Apple's iTunes.

The *Nuclear Wallet Cards for Android* application is designed to work on any size of android device, adapting its user interface to fit any screen orientation, pixel density, and physical dimensions available. A screen-shot from this application can be seen in Figure 2.

FIGURE 2. Screen-shot from INL's Android-based (pre-release) developmental mobile application.

Benefits to DOE

DOE, National Nuclear Security Administration, and its laboratories benefit from the corrections to nuclear data in fission related quantities in several nuclear databases by reducing potential errors in future fission related work. The nuclear data mobile applications benefit the nuclear scientific community by providing a popular data resource in a usable, accessible, mobile device format.

Relevant Publications and Presentations

Piet, S.J., E.A. Hoffman, S.E. Bays, G.E. Matthern, J.J. Jacobsen, R. Clement, and D.W. Gerts, "Fuel Cycle System Analysis Implications of Sodium-Cooled Metal-Fueled Fast Reactor Transuranic Conversion Ratio," *Nuclear Technology*, March 2013. (accepted)

Clements, R., D.W. Gerts, and S. Brown, Erratum to "Nuclear Data Sheets A=233," Nuclear Data Sheets 105 (2005) 109-222. (submitted)

Clements, R., D.W. Gerts, and S. Brown, Erratum to "Nuclear Data Sheets A=232," Nuclear Data Sheets 107 (2006) 2579-2648. (submitted)

Clements, R., D.W. Gerts, and S. Brown, Erratum to "Nuclear Data Sheets A=215, 219, 223, 227, 231," Nuclear Data Sheets 93 (2001) 763-1061. (submitted)

Clements, R., D.W. Gerts, and S. Brown, Erratum to "Nuclear Data Sheets A=230," Nuclear Data Sheets 69 (1993) 155-208. (submitted)

iNWC, Available on Apple's iTunes and App Store.

Treaty Verification with Photo-Induced Prompt Signatures

Mathew Kinlaw, Scott Thompson, and Alan Hunt[1]
12-054

INL is developing nuclear detection technologies for high resolution three-dimensional images of heavily shielded containers to detect, identify, and characterize nuclear materials. In support of the U.S. Government's focus on strategic arms reduction, nuclear material detection technologies are being used for treaty verification and dismantlement applications. While passive inspection techniques have generally been more attractive as candidate solutions, these techniques are limited in their ability to reliably and efficiently detect spontaneous emissions that are either scarce or heavily shielded. By employing an active inspection methodology, additional signatures can be generated and exploited for more robust detection and characterization. This research is examining an active inspection methodology that uses a low-to-moderate-energy bremsstrahlung beam to generate prompt signatures for detecting and characterizing targets of interest. To date, this technique has demonstrated the ability to reliably identify many of the relevant characteristics needed for treaty verification and dismantlement applications.

Summary

During the first year, proof-of-concept measurements were completed to assess the utility of combining gamma-ray signatures with more conventional alternative signatures to produce three-dimensional characterizing images. Using multiple targets positioned at various locations from the inspection source, one-dimensional target localization was demonstrated and readily extended to produce two-dimensional and three-dimensional images. Further, these proof-of-concept measurements demonstrated the technique's ability to discern high-Z targets from their surroundings, and an extended discrimination of fissionable material from other high-Z, non-fissionable material.

With the success of these proof-of-concept efforts, the research focus transitioned to extending the potential fidelity of the technique to include—in addition to fissionable materials—the method's capability for characterizing targets comprised of non-fissionable materials. Figure 1 shows the results of measurements performed on a standard 155-mm artillery shell. These data were generated with the project's novel approach, and were collected with a detector array co-located with the inspection source. Similar to a transmission radiograph, our technique produces a relatively high-fidelity image of a munition (Figure 1). The hollow cavity of the shell's interior is evident (black area at ~520-560 mm), while the grey region towards the rear of the shell indicates a slightly increased wall thicknesses in this area of the shell.
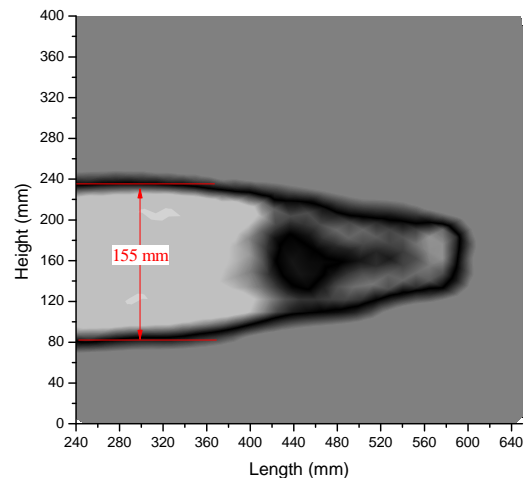
FIGURE 1. Two-dimensional image of a 155-mm artillery shell.

This project continues to successfully demonstrate the ability to detect and localize high-Z materials, and to further discriminate fissionable materials from materials comprised of high-Z, non-fissionable isotopes. Because the spatial resolution of the system (along the beam axis) is dependent on the overall system resolution, the availability of specific dimensions and/or other geometric characteristics can be selected a priori depending on the specific application. In contrast to a transmission radiograph, which generates a response that is an average of all materials along the beam path, our methodology can resolve individual internal features (i.e., multiple successive layers consisting of low- or high-Z materials). For verification applications where high fidelity is sought, or for emergency response applications, this increased resolution is readily possible.

[1] Idaho State University

Benefits to DOE

This research will provide a technical solution applicable to DOE mission objectives for arms control and treaty verification applications. The ability to generate high or low-resolution, three-dimensional images—in addition to unique implementation of radiation signatures—can enable confirmation that treaty limited items presented for inspection are as declared. These same attributes of the technique could also contribute to confirming inspected item types and/or attributing disassembled components. The technology may provide a unique ability to generate high-resolution images for detailed characterization of suspect items for emergency response applications or non-nuclear illicit item characterization (e.g., improvised explosive device detection and/or characterization).

Relevant Publications and Presentations

Kinlaw, M.T., A.W. Hunt, and S.J. Thompson, "Treaty Verification with Photo-Induced Prompt Signatures," *Strategic Advisory Committee, Idaho National Laboratory, Idaho Falls, ID, July 2011.*

Kinlaw, M.T., A.W. Hunt, and S.J. Thompson, "Treaty Verification with Photo-Induced Prompt Signatures," *Photo-Induced Signatures, presented to the BEA S&T Board of Directors, Idaho National Laboratory, Idaho Falls, ID, July 2011.*

Kinlaw, M.T., A.W. Hunt, and S.J. Thompson, "Treaty Verification with Photo-Induced Prompt Signatures," *Strategic Advisory Committee, Idaho National Laboratory, Idaho Falls, ID, June 2012.*

Electronic Energetic Initiation

Michael Daniels, Nikki Rasmussen, Reston Condit, and Michelle Pantoya[1]
12-066

INL is developing systems that can safely and reliably ignite composite energetic materials (CEMs) used in exothermic reactions. The development of such systems requires engineered solutions that prevent inadvertent initiation and assure reliable ignition when desired. This project is focused on understanding the fundamental principles of the initiation energies for various igniter compositions as well as the component designs capable of assuring reliable and stable ignition. Concepts for piezoelectric-based systems were explored, including critical parameters influencing electrical arc ignition, electrical resistivity, and conductivity of particulate mixtures.

Summary

INL investigated CEM response to electrical stimuli and the correlation between the composite's electrical conductivity and ignition sensitivity. The composites consisted of micrometer particle Al combined with another metal, metal oxide, or fluoropolymer. This study also examined the role of fuel particle size on electrostatic discharge (ESD) ignition sensitivity and measured electrical conductance for each CEM. Experimental diagnostics were developed to measure electrical conductivity through a powder media as well as electrostatic discharge ignition sensitivity in terms of minimum ignition energy. Further diagnostics have developed to characterize the piezocrystals and monitor ignition delay time resulting from piezocrystal ignition. Results show a strong correlation between fuel particle size, electrical conductance, and ESD ignition. As fuel particle size is reduced, CEM electrical conductance increases dramatically, as does ESD ignition sensitivity. Electrical conductance increases linearly with increasing Al surface-area-to-volume ratio. This study also examined the electrical conductance and ESD ignition sensitivity of a CEM composed of Al and MoO_3 with varying Al particle size (see Table 1 and Figure 1). These results imply that the microstructure of alumina dispersion throughout the composite may play a role in ESD ignition. Piezocrystals are commonly used for ignition of hydrocarbon fuels, but their application as igniters for solid energetic materials is limited. Examination of piezocrystals as the ignition source for a solid composite energetic material was accomplished by characterizing the piezocrystal's electrical response to mechanical stimuli and coupling these characterizations with the energetic material's ignition sensitivity resulting from the electrical energy generated by the piezocrystal. We developed a diagnostic system that enabled the measurement of ignition sensitivity quantified in terms of ignition delay time and ignition energy (Figure 2).

Experimental results identified: (1) the independence of ignition delay with bulk density is in contrast to observations of ignition delay time via other stimuli; (2) a solid energetic composite can be ignited by a piezocrystal, consistent with electrical stimuli; and (3) ignition delay times are independent of the powder bulk density (Figure 3).

TABLE 1. Results for electrical properties and ESD ignition energy for Al-MoO_3.

Al Avg Diameter (micron)	MoO₃Avg Diameter (nm)	Electrical Conductance at 30% TMD (nS)	Ignition Voltage (V)	ESD Minimum Ignition Energy (mJ)	Electrical Conductivity (nS/m)
20	44	0.00053	>10000	No Ign	0.19
20+30% Al₂O₃	44	0.00008	>10000	No Ign	0.029
4	44	0.11	>10000	No Ign	39.79
4+30% Al₂O₃	44	0.026	>10000	No Ign	9.41
2	44	12.43	2000	4.0	4496.61
0.1	44	210	1000	1.0	75968.55
0.05	44	530	500	0.25	191730.16

[1] Texas Tech University
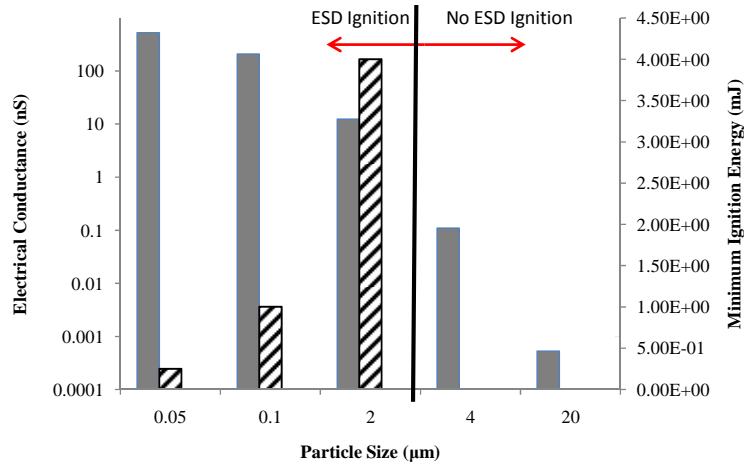
FIGURE 1. Electrical conductance (shaded bar) and minimum ESD ignition energy (stripped bar) for Al-MoO₃ as a function of Al particle size. There appears an ignition threshold associated with Al particle size that occurs between 2 and 4 microns.
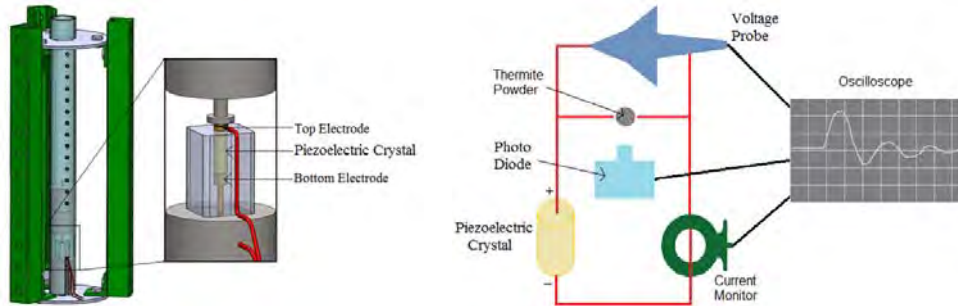
FIGURE 2. Drop test compressed the piezocrystal and generated voltage that ignited a powder mixture – an experimental system used to measure ignition time delay.
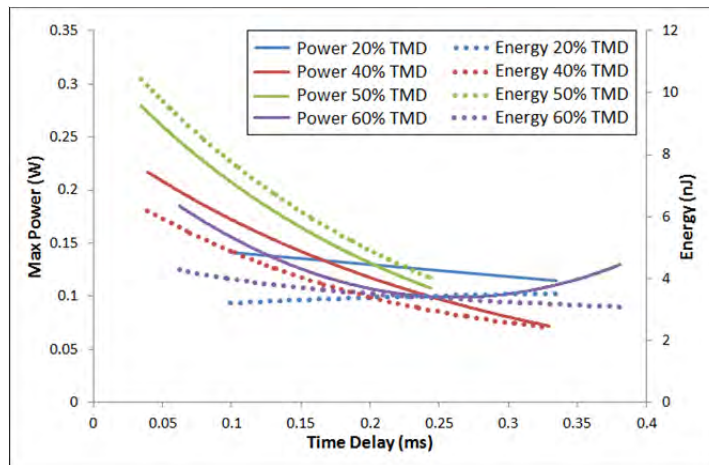
FIGURE 3. Trend lines for maximum power and total energy from the PZT (lead zirconate titanate—one of the most widely used piezoelectric materials) as a function of time delay.

99

Benefits to DOE

This research is focused on increasing the safety of energetic materials' use and field applications of thermite-based energetic reactions for DOE, Department of Defense, and industry. Deployment of these igniter technologies has the potential to significantly increase the reliability of initiation, extend the shelf-life of components, reduce transportation shipping costs and hazards, and minimize the dispersal of hazardous toxic metals.

Relevant Publications and Presentations

Weir, C.M., M.L. Pantoya, and M.A. Daniels, "Electrostatic Discharge Sensitivity of Composite Energetic Materials," Lambert Academic Publishing, (an imprint of AV Akademikerverlag GmbH & Co.), Saarbrucken, Germany, ISBN 978-3-659-22065-4, 2012.

Weir, C.M., M.L. Pantoya, G. Ramachandran, T. Dallas, D.J. Prentice, and M.A. Daniels, "Electrostatic Discharge Sensitivity and Electrical Conductivity of Composite Energetic Materials," *Journal of Electrostatics*, August 2012. (accepted)

Weir, C.M., M.L. Pantoya, and M.A. Daniels, "The Role of Aluminum Particle Size in Electrostatic Ignition Sensitivity of Composite Energetic Materials," *Combustion and Flame*, September 2012. (submitted)

Research on piezocrystal characterization is being prepared for submission to Applied Physics Letters.

Fast Identification of Chemical Warfare Agents, Explosives, and Radionuclides with Lanthanum Bromide Gamma-Ray Detectors

Jayson Wharton, Edward Seabury, and Gus Caffrey
12-069

Since the early 1990s, Prompt Gamma Neutron Activation Analysis (PGNAA) systems have been the mainstay for non-destructive evaluation of suspected chemical munitions for the U.S. Army. A portable PGNAA system allows for fast and accurate assays of unknown munitions that can be conducted in the field with minimal contact between the operators and any harmful chemical compounds or explosives.

PGNAA systems interrogate a suspect munition with neutrons of varying energies that interact with the components on a nuclear level. As a result of the neutron interrogation, both capture reactions (n,γ) and inelastic scattering reactions (n,n') result in the emission of high energy photons.

INL has conducted a series of experiments on different masses of explosive simulants to determine whether using a relatively new type of detector, $LaBr_3(Ce)$, in a similar PGNAA application could significantly reduce detection times for explosives. The current active interrogation system currently uses a High Purity Germanium (HPGe) detector to detect the high energy 10.8-MeV gamma ray from thermal neutron capture on nitrogen to determine the presence of explosives. $LaBr_3(Ce)$ detectors have a similar density to HPGe, a trait necessary to detect high-energy gamma rays, but $LaBr_3(Ce)$ detectors have the additional advantages of being larger, more efficient, and they do not require cooling to liquid nitrogen temperatures.

This project was a one-year study of the feasibility of using $LaBr_3(Ce)$ detectors in a PGNAA system for the detection of explosives by determining the nitrogen peak areas and identification times. An in-depth study of the $LaBr_3(Ce)$ detector response to higher-energy gamma rays or their use in a portable explosive detection system had not previously been conducted, and the use of larger, more efficient lanthanum bromide crystals could potentially speed up explosive detection.

Another aspect of the project was the investigation of spectral unfolding codes. Scintillation detectors, such as $LaBr_3(Ce)$ and NaI(Tl) produce spectra with much lower energy resolution than HPGe. The peaks in these spectra overlap one another for gamma spectra of even moderate complexity. Spectral unfolding involves performing an analysis of these spectra and determining the gamma energy distribution that produced the spectrum.

Summary

To determine whether it is feasible to use a $LaBr_3(Ce)$ scintillation detector in place of the HPGe detector currently used, a series of experimental runs were collected on simulated explosives with each of three different detectors, a 3×3-inch $LaBr_3(Ce)$ detector, a 3×3-inch NaI(Tl) detector, and a 42% relative efficiency n-type HPGe detector. Data were collected using two source-stand configurations, a PGNAA system using an isotopic ^{252}Cf source and a "next generation" active interrogation system which utilizes a Thermo Scientific P385 deuterium-deuterium neutron generator as the neutron source. All resulting spectra were analyzed to determine the net peak counts for both the full-energy 10,829-keV nitrogen peak and its single escape peak at 10,318 keV (Figure 1.)

For the experimental runs, the identification results for the HPGe and $LaBr_3(Ce)$ detectors were very comparable when assaying large amounts of explosive simulant. Both detectors were able to identify large amounts (greater than 20 lb) of explosives quickly and accurately with no false positives for non-explosive materials. As predicted, the larger, more efficient $LaBr_3(Ce)$ detector had peak areas in the nitrogen regions of interest that were a factor of eight to twelve higher than those recorded for the HPGe detector. These higher count rates give encouragement that further development of a $LaBr_3(Ce)$-specific nitrogen-detection algorithm could utilize the increased count rates to decrease the time necessary to identify explosives by an order of magnitude. Future work would entail designing a nitrogen-detection algorithm that is more tailored for use with the $LaBr_3(Ce)$ scintillation detector, rather than utilizing the one currently in use for HPGe spectra.

As part of this project, a brief survey of spectral unfolding codes was also made. It was found that the unfolding with MAXED and GRAVEL package—available from the Radiation Safety Information Computational Center repository at Oak Ridge National Laboratory—provided the necessary functionality for unfolding scintillation spectra. This package was obtained and some limited testing was done. A full unfolding capability of complex PGNAA spectra has not yet been implemented.
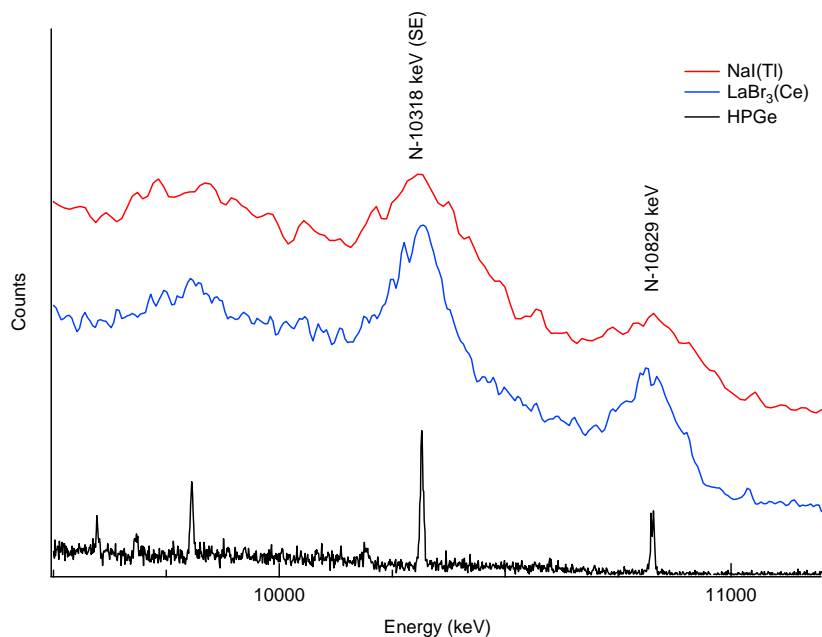
FIGURE 1. A comparison of the response of LaBr$_3$(Ce), NaI(Tl), and HPGe detectors in the nitrogen region of PGNAA spectra.

Benefits to DOE

Speeding up explosive detection is of great interest to the U.S. Army as well as the Defense Threat Reduction Agency, Department of Homeland Security, and DOE National Nuclear Security Administration. Future proposals for outside funding will be/have been enhanced by having the information and tools developed from this LDRD.

Applications and solutions involving gamma spectroscopy that previously would have relied on HPGe detectors could be strengthened by using the lanthanum halide scintillators, in particular for environments where liquid nitrogen cooling is difficult.

Relevant Publications and Presentations

None.

A Nonproliferation-Focused Study and Comparison of the GEANT4 Simulation Toolkit and Monte Carlo N-Particle (MCNP) Functionality, Accuracy, and Development Needs

Scott Thompson, Ryan Clement, and Brian Castle
12-073

The Monte Carlo N-Particle (MCNP) family of codes is the most widely used Monte Carlo tool for modeling fission emissions and their subsequent material interactions, according to the literature. However, for validation and benchmarking reasons it is very desirable to have another internationally recognized and widely used Monte Carlo simulation tool to support national and international nonproliferation research and development. The GEANT4 simulation toolkit is a clear choice because of both its extreme flexibility and its ability to model visible light generation and transport in scintillators, and to more-closely mimic signal generation in solid-state and gaseous radiation detectors. The literature states that GEANT4 has an exceptionally strong history and user base in the high-energy physics regime, yet it has only recently become a commonly used tool in the nonproliferation community.

This project completed a comparison of the GEANT4 simulation toolkit and the MCNP family of codes to establish a validation basis for an internationally-recognized and widely-used Monte Carlo simulation tool to support nonproliferation research and development.

Summary

INL performed several measurement campaigns that were modeled in parallel with both Monte Carlo-based simulation packages. These well-documented measurements all incorporated standard [3]He-based proportional counters and highlighted physical processes that are inherent to nuclear material detection, imaging, radiation dose measurement, and other nonproliferation, safeguards, and security applications. Examples of studied observables are fission reaction emissions (both prompt fission neutron die away and delayed emissions), neutron thermalization rates, and physical detector response. The modeled measurements incorporated electronic neutron generators (both [d,d] and [d,t] reaction generators that produce 2.5-MeV and 14.1-MeV neutrons respectively) as well a [252]Cf isotopic spontaneous fission source. These sources span the energy range applicable to nonproliferation and nuclear safeguards measurements.

Figure 1 is a sample geometry for an active neutron interrogation measurement that was modeled as a part of these efforts. In this geometry a large challenge pallet comprised of solid shielding material with a compartment at its center for holding special nuclear material (SNM) is irradiated with neutrons. The detectors positioned adjacent to the pallet monitor for the emission of fission signatures that indicate the presence of fissionable material. This figure also demonstrates the advantage of using GEANT4 visualization capabilities to illustrate and communicate problem geometries. The orange tracks in this geometry denote neutron trajectories, while the blue represent those of gammas. Yellow dots indicate particle interaction points.
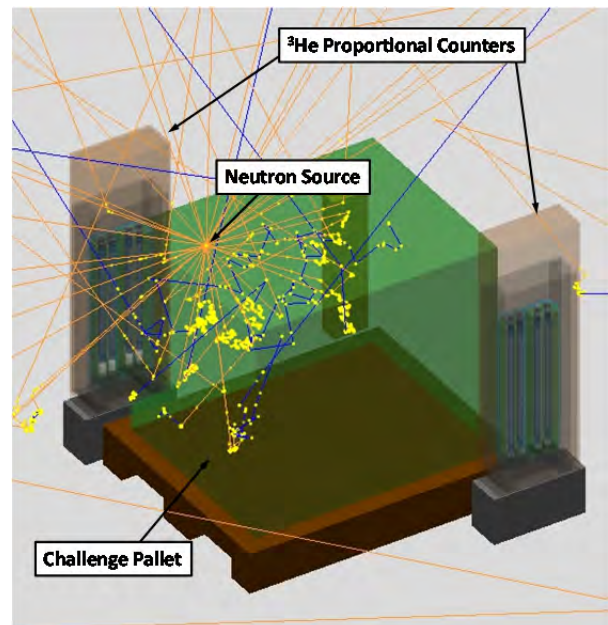
FIGURE 1. An example of a modeled measurement geometry.

All results from the simulation campaign are currently being collected and assimilated for an upcoming journal publication. However, the effectiveness and utility of GEANT4 as a nonproliferation application modeling tool is made evident in the preliminary analyses.

Benefits to DOE

This study is of direct benefit to DOE's national security mission by aiding in the development of new detectors and detection systems for nuclear nonproliferation and counterproliferation measurements related to advanced safeguards, nuclear forensics, emergency response, and nuclear material detection.

Relevant Publications and Presentations

Clement, R., "A Nuclear Science Education Course Proposal: Modeling Radiation Transport and Detection in Experimental Apparatus with the GEANT4 Simulation Toolkit," *University and Industry Technical Interchange (UITI2011) Review Meeting in Oakland, CA, December 6, 2011.*

Demonstration of Total Ion Control (TIC) Technology

Jill Scott, Timothy McJunkin, and Gary Groenewold

12-081

Many analytical instruments, such as mass spectrometers (MS) and ion mobility spectrometers (IMS), rely on the ability to manipulate and detect charged particles (i.e., ions). Most of these instruments have relatively large footprints and power requirements. Attempts at making them deployable in truly miniature formats for terrestrial or extraterrestrial applications are fraught with technical challenges, particularly when the process requires atmospheric generation on ions with subsequent insertion of ions into an instrument operating in a vacuum. Complicated ion optics with multiple electrode and insulator parts and associated electrical contacts and circuitry are state of the art for current commercialized instruments. These ion optic systems are inefficient for introducing ions from atmospheric pressure into instruments because many ions are lost through collisions with the electrode surfaces. A common method used to minimize this problem is to employ high air flow, which is achieved by using large vacuum pumps. But this approach increases the footprint and power consumption of the instrument. In cases where gas flow is an issue, the drawbacks are even greater because the flow is complicated due to the edges of the many conductors and/or insulators that may cause turbulence. These problems result in very low efficiency for ion transmission, which limits the sensitivity of instruments, particularly miniaturized mass spectrometers.

There is thus an important need for ion optic technologies that have efficient ion transmission to maximize collection and detection. Total ion control (TIC) technology is a radically simple, robust concept for creating devices to control ion trajectories using resistive or semiconductive materials (i.e., no longer just electrodes and insulators), so that more creative solutions can be developed that operate at lower power, enabling instruments to be miniaturized. Because complicated ion optics can be created from one resistive piece that only requires two electrical contacts, TIC-based ion optics are very robust. Because MS and IMS instruments are ubiquitous analytical tools that use ion optics, there are a host of applications that will benefit from TIC technology and provide INL and DOE with capabilities not available elsewhere. A means for high efficiency insertion of ions from various ionization sources (e.g., electrospray and laser desorption) would have high value to diverse fields ranging from environmental, homeland security, nuclear nonproliferation, pharmaceutical, medical and space exploration applications.

Summary

Many MS instruments rely on electrospray ionization (ESI) and desorption electrospray ionization (DESI); therefore, a new TIC ion inlet device was designed and fabricated for a commercial LCQ-DECA-MS (Thermo-Finnigan™). The inclusion of DESI is important because this technique is known to have very poor ion transfer as it is currently practiced. Additionally, the instrument was equipped with the ability to move the ionization source relative to the mass spectrometer inlet in a controlled manner because commercial ESI-MS instruments are relatively sensitive to source-inlet alignment. The electrostatic field produced by the TIC inlet is more robust and efficient for guiding the ions into the mass spectrometer.

As an example of the advantage TIC can provide, the instrument was operated both in its original configuration in standard ESI mode without the TIC inlet as well as with the TIC inlet for comparison purposes (Figure 1). Tetraoctyl ammonium bromide in a 50:50 mixture of methanol and water was used as the sample because it gives a simple mass spectrum with a peak at m/z 466. The abundance or signal intensity of the peak was measured as the source was moved laterally away from the inlet of the mass spectrometer. Typically, in scientific experiments comparing one method to another, it is desirable to keep all of the parameters the same except for one. Because the TIC inlet is radically different, many parameters must be changed to optimize the signal for TIC. The TIC parameters are deleterious to obtaining a signal in standard ESI mode, to the point that there may be no signal at all when using the commercial ESI inlet. Thus, determining the best conditions for the comparison is difficult. However, the converse situation is not quite as bad in that, while optimization for standard ESI does not produce the most intense signal with the TIC inlet, there is still a signal. Therefore, the logarithmic plot in Figure 1 is actually biased toward standard ESI as opposed to the TIC setup. In Figure 1, the signal intensity of m/z 466 drops off dramatically as the source is moved away from the inlet with the standard ESI setup. With the TIC inlet, the signal remains high even with large displacements demonstrating that the TIC inlet provides a more robust, efficient electrostatic field for collecting and guiding ions into the mass spectrometer inlet.

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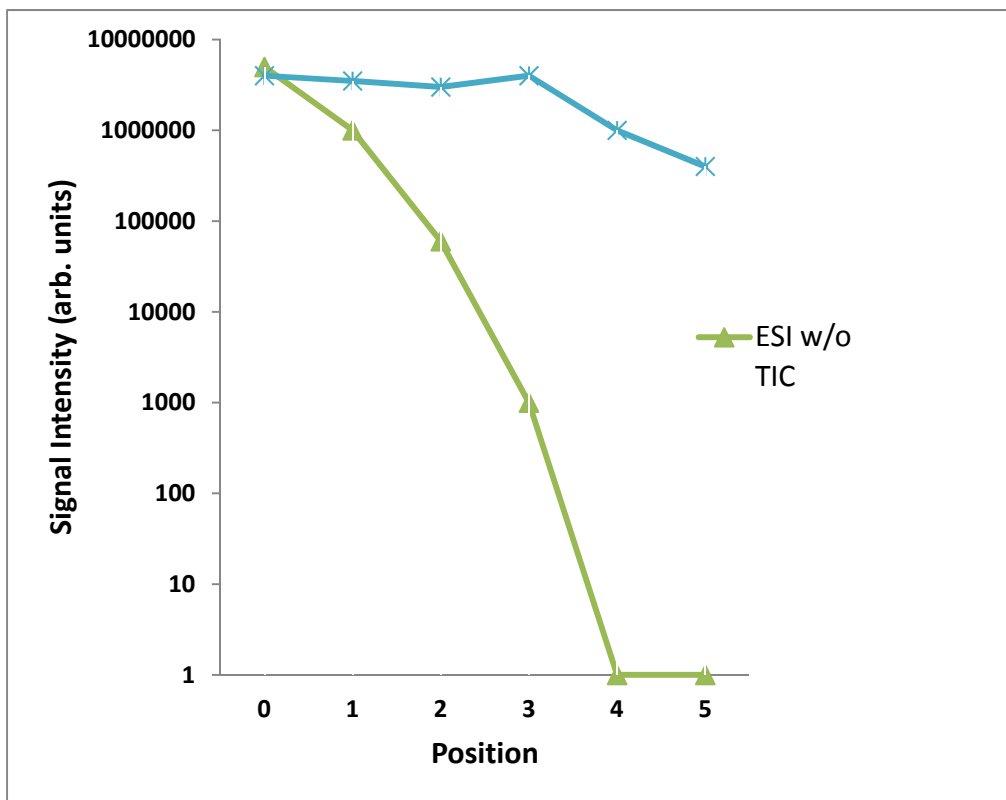
FIGURE 1. Graph of signal intensity versus lateral position for an ESI-MS without (Δ) and with (*) a TIC-based inlet. The standard ESI-MS signal drops off logarithmically as the ionization source is moved relative to the inlet, while the signal for the TIC-based inlet remains robust even when the ionization source is misaligned by several millimeters.

Benefits to DOE

TIC technology provides significant improvement in detection limits and miniaturization of analytical instruments, such as mass and ion mobility spectrometers. Improved, less expensive miniaturized instruments enabled by TIC would have application in nuclear nonproliferation because these instruments could be employed by International Atomic Energy Agency inspectors for detecting potential violations. Because TIC technology will help produce less expensive, lighter weight, robust miniaturized analytical instruments, it can also facilitate field monitoring for environmental contamination, exploration for oil and mining (e.g., rare earth elements), and detection of explosives and chemical warfare agents. Additionally, less expensive instruments will allow industries to deploy more on-line, in situ monitoring of processes that will provide timely information to assist plants in minimizing waste generation. TIC also has the potential to radically improve remote instruments, such as those for space exploration. Thus, TIC is a fundamental technology with wide ranging applications of interest to government agencies such as DOE, Environmental Protection Agency, Defense Advanced Research Projects Agency, and National Aeronautic and Space Administration (NASA).

Relevant Publications and Presentations

Scott, J.R., T.R. McJunkin, and G.S. Groenewold, "Ion Inlet Design for Improved Ion Transmission Efficiency for Electrospray Ionization Mass Spectrometry (ESI-MS)," *International Journal of Mass Spectrometry,* 2012. (in preparation)

Multi-Modal Radiation Detection for Nuclear Nonproliferation and Treaty Verification

Ryan Clement, David Gerts, and Richard Metcalf
12-092

This project designed a conceptual experimental novel radiation detector system based on commercially available components. The Monte Carlo Neutral Particle (MCNP) family of codes was used to begin a simulation effort to better understand the performance of a detector, if one is built. The central theme of this project is to develop a novel radiation detector concept capable of distinguishing gamma-rays and neutrons while potentially providing directional information for security inspections and emergency response.

Summary

This project was established to complete a system design and understand the conceptual performance of the proposed detector through modeling and a review of performance of other detection systems. The proposed system design focused on the special application needs of locating illicit nuclear materials in real-world environments related to, for example, event surveys or incident response. The design included concepts for use of the exceptionally high neutron capture capabilities of the naturally occurring, stable isotopes of gadolinium, shown in Figure 1 and with other popular nuclides used for neutron detection. The goals were to achieve high detection efficiency, radiation discrimination, source direction, and miniaturization.

With regard to system design, a conceptual experimental system was designed based on commercially available components, a key benefit of this proposed system. The MCNP family of codes were used to begin a simulation effort to aid in understanding the performance of a detector should one be built.

To resolve optimal performance characterization of the detector, peer review was undertaken with the Defense Threat Reduction Agency, the United States Air Force (USAF), and Los Alamos National Laboratory. The system concept has potential value in space system applications and is under consideration by the USAF along with research collaboration with Los Alamos National Laboratory. A publication related to the Monte Carlo analysis conducted as a part of this work is being prepared with submission planned for this fall to an appropriate professional, peer-reviewed journal.
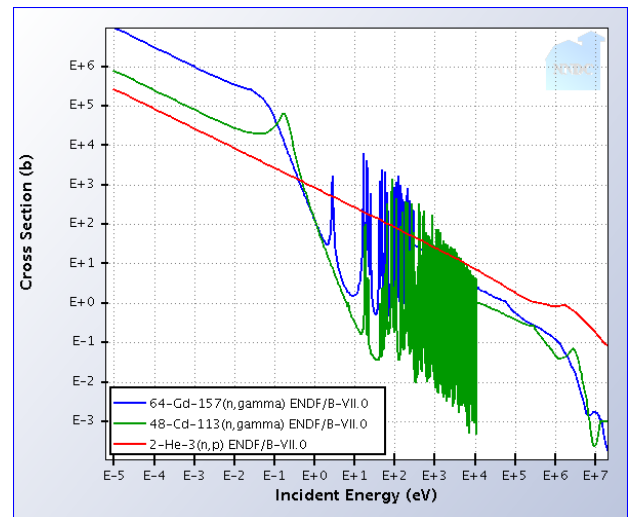
FIGURE 1. Stable isotopes of gadolinium.
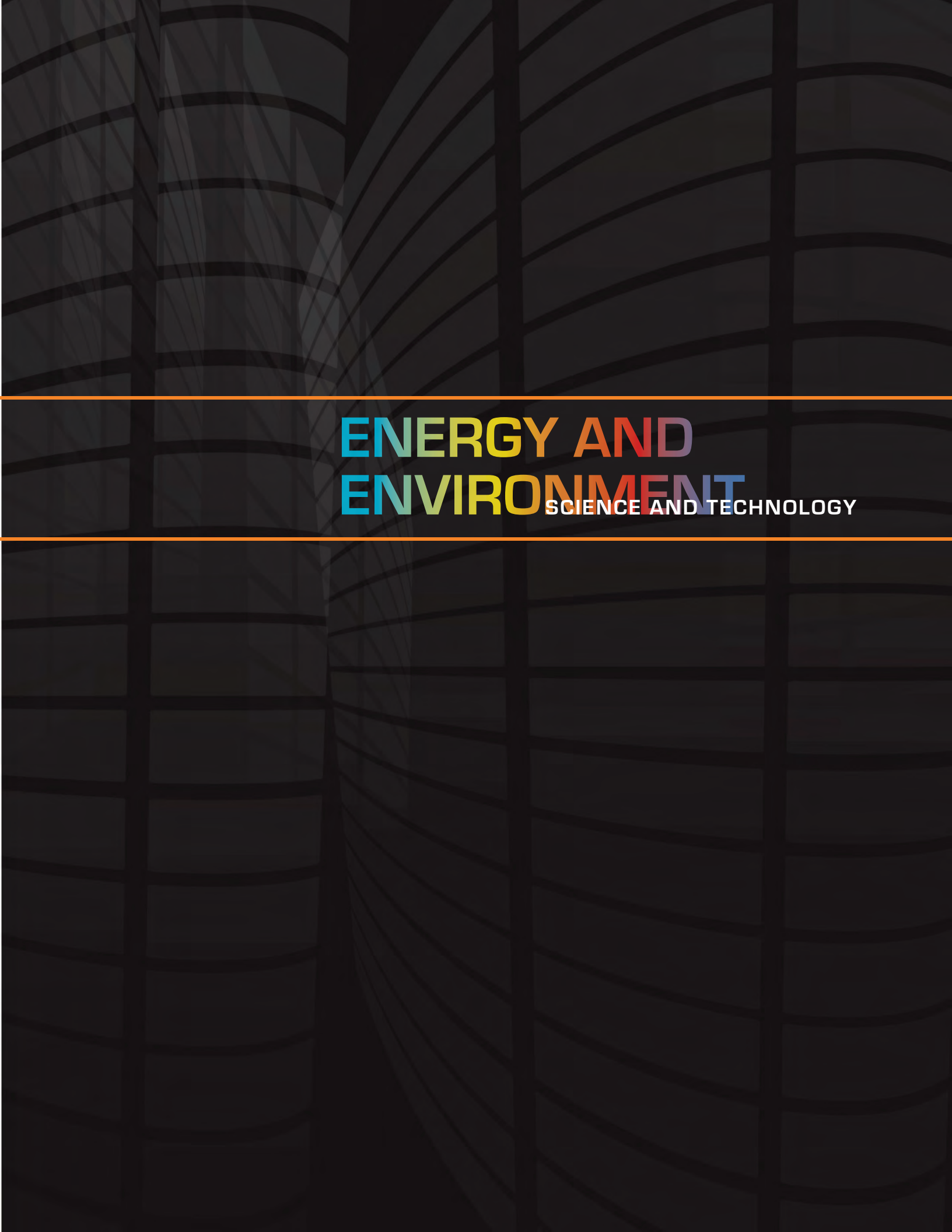
Benefits to DOE

The main benefit of this research to the DOE's National Nuclear Security Administration, and the Department of Defense, is in providing necessary and effective radiation detection equipment to national emergency responders and security inspectors. Additionally, the detector concept is described in an INL invention disclosure record.

Relevant Publications and Presentations

Publication to an appropriate, professional, and peer-reviewed journal is planned.

Clement, R.R.C and D. Gerts, "WARLOC: An Efficient Neutron and Gamma Radiation Location System," to Defense Threat Reduction Agency, 2012.

ENERGY AND ENVIRONMENT

SCIENCE AND TECHNOLOGY

Degradation and Conversion of Lignin Using Extremophilic Systems

William Apel, John Aston, Jeffrey Lacey, Brady Lee, Deborah Newby, David Reed, David Thompson, and Vicki Thompson

10-011

Lignins are a significantly underutilized waste product in biomass processing, and as such represent a largely untapped resource. The goal of this project is to assess the use of extremophilic systems for the bioconversion of lignin to feedstocks and value-added products. This research seeks to characterize the presence and activity of bacterial lignin degradation systems in acidic and alkaline hot springs by: (1) isolating and characterizing microbial isolates from alkaline hot springs in the Alvord Desert (AD) of Oregon and Yellowstone National Park (YNP); (2) characterizing lignin degradation activity by the thermoacidophile *Alicyclobacillus acidocaldarius*, isolated from a geothermal source in YNP; and (3) mining metagenomic data collected from hot springs in the AD and YNP. This research requires an interdisciplinary approach integrating microbiology, genetics, biochemistry, and metabolomics. A combination of these methods is necessary to fully characterize the lignin degradation potential of these extremophilic systems. Completion of this work will lead to the identification and isolation of industrially important thermo-stable bacteria and/or enzymes with applications in converting lignocellulosic compounds to sugars and other chemicals for downstream processes, such as fermentation.

Summary

Isolation and characterization of microbial strains—*Thermus thermophilus* ST and S42 were isolated from high pH (9) and temperature (70°C) hot springs in the AD and the Heart Lake Geyser Basin in YNP. The two strains exhibited lignin degrading potential at pH 9 and 70°C, due to their ability to use the lignocellulose degradation products kraft lignin, ferulic acid, cinnamic acid, and *p*-coumaric acid for growth (Figure 1). Growth on the soluble fraction of alkaline pretreated lignocellulose sources, corn stover, corn cob, and lodge pole pine was evaluated. The dye decolorizing activity was confirmed with Remazol Brilliant Blue R, an industrial dye and lignin analog compound. In addition, laccase mediated 2,2'azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) activity was observed for both isolates when 0.05 mM $CuSO_4$ was supplemented to the growth medium. Ligninolytic bacteria capable of growth at pH 9 and 70°C are useful in conjuncture with an existing alkaline lignocellulose pretreatment method to depolymerize and remove lignin prior to the production of second generation biofuel. Growth on aromatic lignin precursors, such as

ferulic acid, innamic acid, and *p*-coumaric acid is important because these phenolic compounds are the building blocks and common degradation products of lignin. Positive effects on growth suggest these strains would not be inhibited by the secondary production of these compounds during bioprocesses.
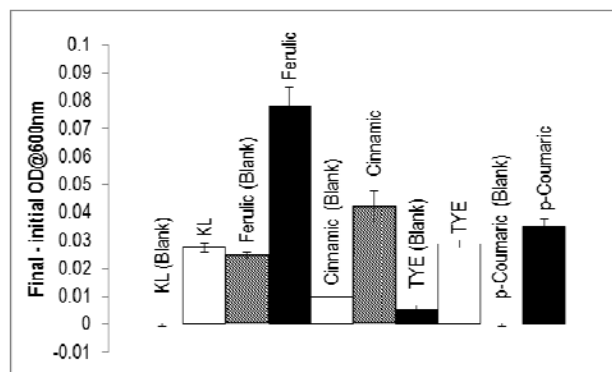
FIGURE 1. Growth of *T. thermophilus* S42 on lignin and lignin precursors.

Characterization of A. acidocaldarius—Experiments were conducted to characterize the ability of *A. acidocaldarius* to affect lignin, the effect of lignin degradation byproducts on its growth, and its ability to degrade such byproducts. Experimental results suggest that *A. acidocaldarius* may affect lignin to some extent (as measured by optical density at 280 nm after various levels of filtration). These effects increase significantly in the presence of 100 µM copper, suggesting that putative copper oxidases identified in the genome of *A. acidocaldarius* may exhibit activity on lignin. These effects were more pronounced when soluble lignin was used. However, *A. acidocaldarius* also appeared to partially solubilize insoluble lignin sources. In addition, to affecting lignin, the presence of copper enabled *A. acidocaldarius* to degrade inhibitory concentrations of phenolic acids (1 g/L) to between 100 and 500 mg/L, allowing more rapid growth of *A. acidocaldarius.* This is an important consideration as such compounds may inhibit downstream processes that convert lignin-derived sugars into alcohols or other value-added products. An example of such data is shown in Figure 2. Finally, enzyme assays were used to identify activities on ABTS that were increased by the presence of copper. Maximum enzyme activity was noted over a temperature range from 60–70°C.

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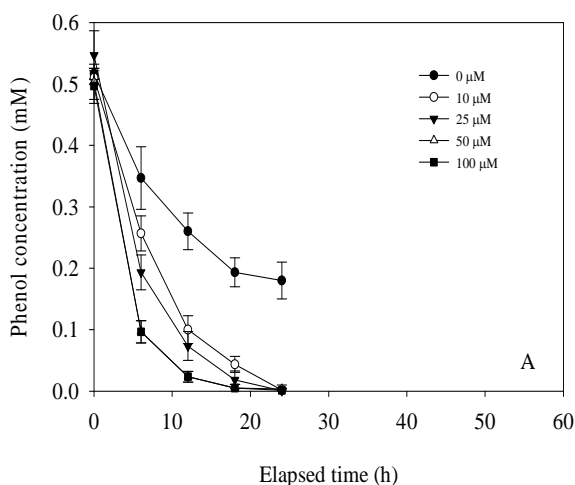
FIGURE 2. Degradation of phenol by *Alicyclobacillus acidocaldarius* in the presence of various concentrations of μM copper.

This research project has supported the research of a student for the completion of a Master's of Science (MS) degree at Montana State University. The student completed her degree in May and received her MS in Chemical and Biological Engineering.

Metagenomic Analyses—Samples from AD and YNP hot springs were collected, and metagenomic DNA was extracted and amplified. This DNA was then sequenced by Eurofins MWG|Operon. Bioinformatic tools have been applied to compare this metagenomic data against known databases for enzymes relevant to lignin degradation. These comparisons suggest the presence of several enzymes related to the oxidation of lignin and lignocellulosic compounds, including laccases, amylases, cellulases, hemicellulases, oxidases, and peroxidases. In addition, a database has been constructed from the metagenomic data against which specific enzymes of interest may be compared.

Benefits to DOE

This conversion of lignin to value added chemicals will help in decreasing our reliance on foreign fossil fuel reserves, which is a goal of the DOE's energy security mission.

This LDRD project will also expand our expertise in extremophilic enzymes related to the processing of

biomass for fuel and chemical feedstocks, which supports the DOE's energy security mission. Currently, biorefinery lignin is burned to generated heat, wasting carbon that could be used for chemical production while generating CO_2. Extremophilic enzymes developed during this project could allow conversion of carbon locked up in the lignin structure to feedstocks for chemical production that typically relies on fossil fuels. In addition, the enzymes developed could be added to stored plant biomass prior to pretreatment and conversion to ethanol, potentially decreasing pretreatment time and severity of the process, which will also bring down the cost of bioethanol production.

Relevant Publications and Presentations

Aston, J.E., B.D. Lee, J.A. Lacey, D.T. Newby, D.W. Reed, D.N. Thompson, V.S. Thompson, and W.A. Apel, "Degradation of Phenolic Compounds by the Thermoacidophile Alicyclobacillus Acidocaldarius," 2012. (in preparation)

Aston, J.E., B.D. Lee, J.A. Lacey, D.T. Newby, D.W. Reed, D.N. Thompson, V.S. Thompson, and W.A. Apel, "Effects of Phenolic Compounds on the Growth of Alicyclobacillus Acidocaldarius," 2012. (in preparation)

Aston, J.E., B.D. Lee, J.A. Lacey, D.T. Newby, D.W. Reed, D.N. Thompson, V.S. Thompson, and W.A. Apel, "Effects of Organic Acids on the Growth of the Hemicellulose and Cellulose Degrading Thermophile, *Alicyclobacillus acidocaldarius*," 2012. (in preparation)

Aston, J.E., B.D. Lee, J.A. Lacey, D.T. Newby, D.W. Reed, D.N. Thompson, V.S. Thompson, and W.A. Apel, "Metabolic Model to Predict the Conversion of Glucose and Xylose by the Thermophilic Acidophile *Alicyclobacillus acidocaldarius*," 2012. (in preparation)

Lee, B.D., W.A. Apel, J.E. Aston, M.R. Walton, and R. Carlson, "Potential for Production of Metabolites by *Alicyclobacillus acidocaldarius,*" Society for Industrial Microbiology and Biotechnology Meeting, New Orleans, Louisiana, July 2011. (invited)

Popovitch, A.E., B.D. Lee, J.E. Aston, B.M. Peyton, and W.A. Apel, "Isolation and Characterization of Thermophilic, Lignin-degrading, Alkaline-tolerant Bacteria," *11th International Conference on Thermophiles Research, Big Sky, MT, September 2011.*

Peterson, J., B.D. Lee, and J.E. Aston, "Comparison and Distribution of Insertion Sequences in Alicyclobacillus Acidocaldarius with Environmental Isolates and Type Strains," *Idaho National Laboratory, Student Research Expo, Idaho Falls, ID, August 2011.*

Aston, J.E., B.D. Lee, J. Lacey, D.T. Newby, D. Reed, D.N. Thompson, V.S. Thompson, and W.A. Apel, "Degradation and Conversion of Lignin Using Extremophilic Systems," *Idaho National Laboratory Professional Exchange, Idaho Falls, ID, August 2011.*

Feedstock Processing and Energy Storage

Humberto Garcia, Lee Shunn, and Richard Boardman
10-059

Liquid fuels constitute an important potential product set due to their ubiquity in transportation and power generation applications. Amongst liquid fuels, methanol can be used as an ultra-clean synthetic fuel and is competitive with many alternatives in terms of combustion efficiency and mileage. Methanol can also be used as a feedstock for other chemical processes, including methanol-to-gasoline (MTG) plants and dimethyl ether (DME) production for clean diesel applications.

This synthetic fuel experiment was designed as a laboratory-scale demonstration of fuel production relevant to integrated energy systems. The experiment combines a modular electrolysis unit for hydrogen production and a catalytic synthetic-fuel reactor to produce high-quality liquid transportation fuels. In its current configuration, the synfuel test bed can synthesize liquid methanol from a carbon feedstock (containing CO gas) and water. The facility has been implemented to flexibly accommodate investigations of other chemical reactions and product separation technologies.

Summary

The experimental apparatus (see Figure 1) was designed, installed, and operated for more than 100 hours of testing and produced more than 6 liters of liquid methanol. The results presented here are from "once through" tests, where the recycle compressor was disabled and product gases were directed to the exhaust vent after flowing through the reactor only once. The composition of the liquid products was analyzed offline using gas chromatography (GC). The liquid samples contained approximately 98% methanol (by mole), with the remaining 2% composed of higher alcohols mostly ethanol, dimethyl ether, and methyl formate.

Data from a typical day of operations are shown in Figure 2, where composition measurements are reported on an "argon free" basis. The temperature signals, T1-T6 represent measurements from the six thermocouples located along the length of the reactor. T1 indicates the measurement station nearest the reactor inlet, and T6 is the station nearest the outlet. The reactor chamber was mounted vertically in the system, with gas flowing from top to bottom. This orientation led to some settling of the catalyst particles during installation and testing. Consequently, T1 seems to be located outside the packed bed in the void space above the catalyst and reports much lower temperatures than T2-T6.
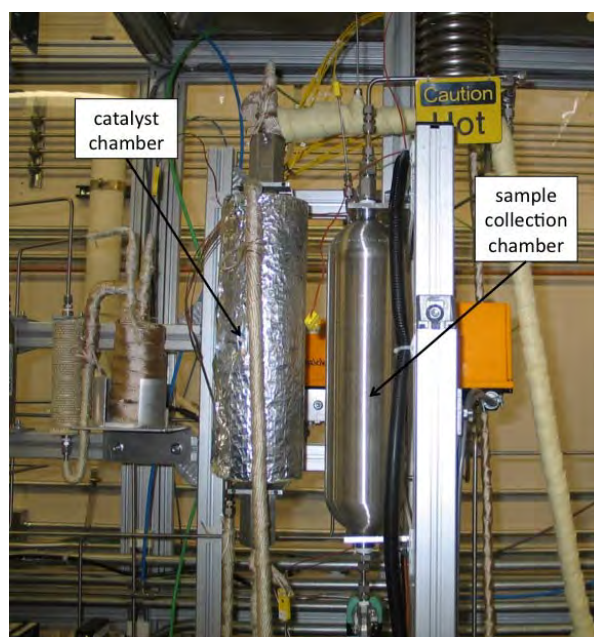
FIGURE 1. Experimental apparatus.

Each testing sequence for the methanol reactor was coordinated to fit roughly into one extended working day period. Transients from the initial startup lasted approximately 150 minutes from the beginning of the temperature ramp. For the data in Figure 2, steady operations were maintained throughout the rest of the test period. Other test sequences (not reported here) were executed to examine the dynamic response of the reactor system to changes in operating conditions such as temperature, pressure, and flow rates. These data are being used to validate and improve models and control systems for integrated synfuel processes.
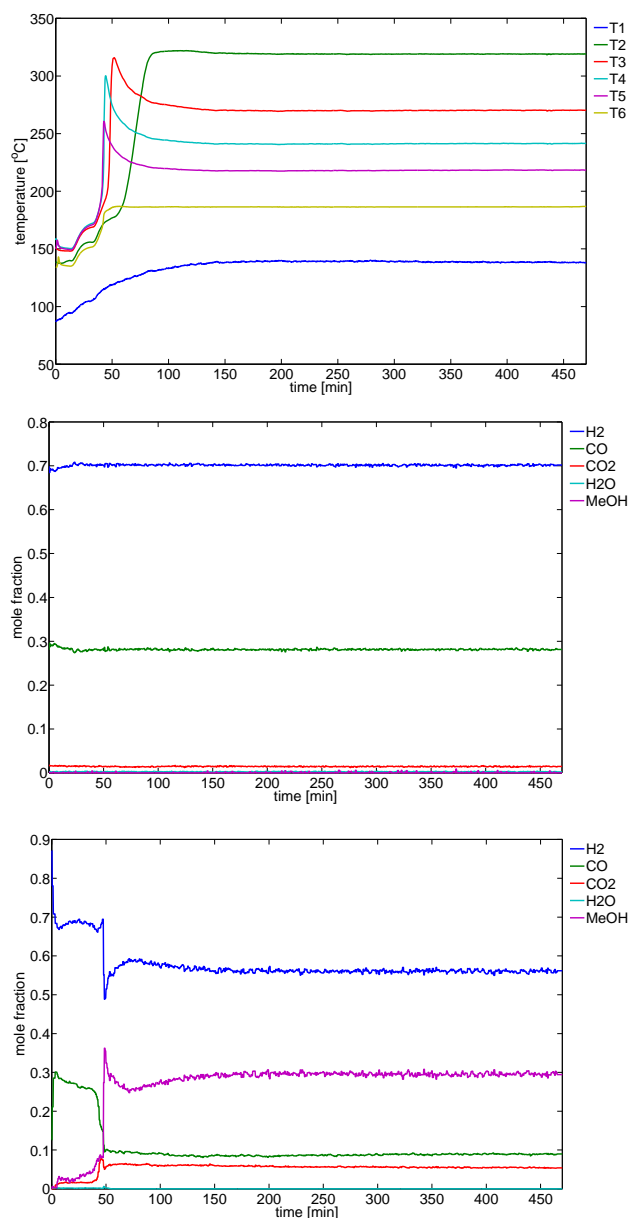
FIGURE 2. Synthetic fuel reactor temperature profile (top), inlet composition (middle), and outlet composition (bottom) during steady methanol production.

Benefits to DOE

Integrated energy systems that can dynamically alter their production mode to deliver power, heat, or chemical products offer a pathway to operate independent and sustainable energy "islands" by improving the utilization of fossil resources, reducing greenhouse gas emissions, and stabilizing contributions from renewables. These hybrid systems can divert resources during periods of low electrical demand to produce chemical products, such as hydrogen or transportation fuels, that can be stored to balance future supply shortages or to power offline applications. This capability supports the development of modular dynamically operable energy conversion and energy storage systems. The experimental capability includes high pressure hydrogen production, syngas (CO and H_2) compression and recirculation, synfuels production, and by-product gas management. In addition, development, testing, and demonstration of a new real-time monitoring Raman spectrometer probe were completed in FY 2012. This probe will enable advanced diagnostics and prognostics for control of a distributed small-scale system.

Remote, automatic monitoring, and control is a significant technical barrier to the operation of small modular distributed synfuels production. DOE and industry have recognized that small modular conversion plants need to be developed to better exploit remote and stranded energy assets, such as natural gas, that is co-produced with oil in remote environmentally sensitive locations. The capability provides a test bed to demonstrate several key principals including: (1) remote conversion of electricity and carbon-based resources into synfuels, (2) modular, deployable energy conversion system technical and economic feasibility, and (3) remote monitoring and control using real-time system.

Relevant Publications and Presentations

None.

Water and Energy System Interdependency Modeling for Multicriteria Decision Analysis

Robert Jeffers, Jacob Jacobson, and Andrew Ford[1]
10-065

Complex feedback between various uses of water has not been adequately accounted for when planning energy development. This project has improved holistic value of energy development strategies by integrating management criteria for water availability, water quality, and ecosystem health into the energy system planning process. The goals of the project were met by developing a simulation framework that includes the system-level feedbacks between long-term electricity planning metrics and long-term water planning metrics. The Snake River Basin (SRB) in southern Idaho was used as a case study to show options for improving full economic utilization of aquatic resources given multiple scenarios such as changing climate, additional regulations, and technology development. Through the incorporation of multiple management criteria, potential crosscutting solutions to energy and water issues were developed. The final result of this work is the Water and Energy Systems Tool (WEST), which is a water and energy modeling framework that can develop immersive, stakeholder-inclusive simulations for which questions about long term energy-water management strategies are the primary topic. These simulations can then be published online and shared to create a forum for energy and water system management that better includes the response of humans to drivers of change.

Summary

The WEST framework was completed using a new approach to the system dynamics methodology termed *object-oriented system dynamics*. Four components, or WEST *objects*, were designed: a natural hydrology component, an irrigated agriculture component, a managed reservoir component, and a groundwater aquifer component. These components all have similar spatial and temporal resolutions, namely large watersheds (tens to hundreds of thousands of acres) and average monthly behavior. By linking objects together, specifying their parameters, and calibrating them to observed data, a proof-of-concept WEST model was developed that shows excellent fit to observed stream flows and reservoir storage in the SRB (Figure 1). This type of model represents a step forward in the coupling of dynamic surface water, ground water, and human behavior models. It can be viewed as a hybrid between stakeholder-oriented

modeling and process-oriented modeling. Because WEST uses only precipitation and temperature as inputs, and because it incorporates a user-friendly interface, testing basin-wide responses to drivers such as climate change or managed aquifer recharge requires significantly less effort than similar state-of-the-art models. This ease of operation can greatly decrease the effort required in creating long-term climate change mitigation and adaptation strategies.

To increase stakeholder involvement in the development process and to improve outreach capabilities, WEST models were published to an online geographic information system (GIS)-enabled interface. This interface was custom designed such that any simulation built using the PowerSim modeling environment can be linked to a GIS display and may be run, controlled, or explored by online users. This leap forward in ability has generated interest from PowerSim's developers as well as the general system dynamics community.

Using the WEST proof-of-concept model of the SRB, projections of hydropower generation in response to projected climate change scenarios were completed. These projections were then fed to Washington State University's Western Energy Coordinating Council and Independent Power Company (WECC-IPC) model, which includes the behavior of retail electricity prices given information about generator availability and cost throughout the western United States. WEST projects that a 3°C rise in temperature in the SRB may be accompanied by a 10% yearly decrease in hydropower generation. Furthermore, the WECC-IPC model projects this decrease in hydropower generation may cause a 15% increase in retail electricity rates over a twenty-year period. These retail rates are then fed back to WEST to examine the impact on agricultural production in the SRB.

WEST also has been used extensively to increase outreach between INL and decision-making agencies in the water and energy realms. In recent meetings with the Idaho Department of Water Resources, the WEST SRB model was used to experiment with strategies to stabilize declining aquifer levels. Idaho Department of Environmental Quality commented that WEST would aid them in understanding the impact of stream flow

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[1] Washington State University
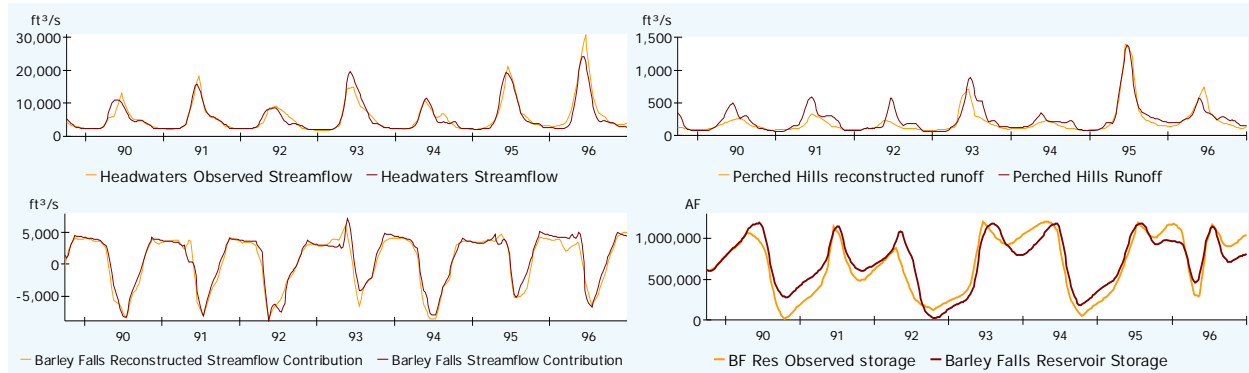
FIGURE 1. The WEST proof-of-concept fits well to observation, as illustrated by a seven-year simulation including four hydrologic targets (clockwise from top left): stream flow, natural runoff, catchment-wide water balance, and reservoir storage.

projections on the Total Maximum Daily Load regulatory process. The Idaho Public Utilities Commission has acknowledged that WEST would be helpful to increase understanding of the dependency of electricity prices on hydrologic conditions.

This project has funded two summer undergraduate interns over its lifetime. It has fostered a relationship between INL, Washington State University, and the University of Idaho for collaborative water and energy resources research. In the summer of 2012, interest in WEST spurred the first annual meeting of Columbia Basin hydrologic systems modelers in Boise, ID. This project partially funded the Ph.D. research for Mr. Jeffers, which will be complete in January 2013. At least two peer-reviewed journal articles are planned to be submitted at that time.

Benefits to DOE

WEST will benefit DOE by providing an unbiased forum to include the most relevant stakeholders in integrated planning for water and energy resources. WEST can be used for a host of DOE-relevant studies going forward, including the impact of climate change on fossil energy cooling systems, the collective impact of increased natural gas production on future water availability and quality, or inter-state issues regarding equitable allocation of water resources. Because WEST can be published online, it offers an opportunity for collaborative water and energy model-building that would bring together widely dispersed DOE-funded researchers. Outside of DOE, WEST is highly relevant to the Department of Interior and the U.S. Army Corps of Engineers for assessing reservoir

management plans to provide flood control and/or agricultural water supply. WEST can be used by the Department of Homeland Security to address long-term risk of municipal water supplies and response of communities to drought or flood.

Relevant Publications and Presentations

Jeffers, R., J. Jacobson, and K. Scott, "A Framework for Analysis of Energy-Water Interdependency Problems," *Proceedings of the International System Dynamics Conference, Washington, D.C., July 24–28, 2011.*

Jeffers, R., A. Ford, and J. Jacobson, "Projections of Electricity Market and Agricultural User Behavior Given Climate Change Scenarios in the Snake River Basin," 2013. (in preparation)

Jeffers, R., J. Adam, J. Jacobson, A. Ford, A. Beall, and K. Cafferty, "The Water and Energy Systems Tool: A Modeling Framework for Integrated Water and Energy Planning," 2013. (in preparation)

Jeffers, R., "A Dynamic Modeling Framework for Integrated Energy and Water Resource Planning," Dissertation to be submitted to the School of Earth and Environmental Sciences, Washington State University, Pullman, WA, 2013.

Jeffers, R., P. Wheatley, J. Jorge, and G. Matthern, "Spatial and Temporal Modeling of the Energy Water Nexus," Presentation to State Agencies, Boise, ID, 2010.

Cleveland, A., J. Jacobson, and R. Jeffers, "Using System Dynamics for Hydrologic Management of Palisades Reservoir," poster for the 2010 INL intern expo, 2010.

Jeffers, R. and J. Jacobson, "A Framework for Analysis of Energy-Water Interdependency Problems," *2011 Boise Western Energy Policy Research Conference, Boise, ID, August 25–26, 2011*.

Rowse, A., J. Jacobson, and R. Jeffers, "Heading WEST: Water and Energy Scenario Testing," Poster for the 2011 INL intern expo, 2011.

Jeffers, R. and J. Jacobson, "The Water and Energy Systems Tool (WEST): Project Summary," *EES&T External Peer Review and the 2011 Idaho Water Seminar, Idaho Falls, ID*, 2011.

Jeffers, R., M. Overton, and J. Jacobson, "Demonstration of a Web-Based Geospatial System Dynamics Tool," *Online presentation to international industry colleagues, February, 2012*.

Jeffers, R., M. Overton, and J. Jacobson, "Water and Energy Scenarios Testing (WEST): Basin-Wide Socio-Hydrologic Water Balance for Integrated Water Resource Planning," *2012 Mountain West Water Institute Waters of the West Workshop, Idaho Falls, ID*, 2012.

Jeffers, R., M. Overton, and J. Jacobson, "Water and Energy Scenarios Testing (WEST): Developing Toolsets for Integrated Water and Energy Resource Planning," *2012 Universities Council on Water Resources (UCOWR) Annual Conference, Santa Fe, NM, July 17–19, 2012*.

Hybrid Systems Process Integration and Dynamics Studies

Robert Cherry, Michael McKellar, and David Muth

10-067

Hybrid energy systems (HES) (systems that combine multiple energy production systems—such as nuclear, coal, biofuels, wind, and/or fossil fuels) have the potential to change the economics of energy production. This three-year project has focused on exploring the characteristics and potential benefits of hybrid systems. Our focus has included technical, economic, and environmental factors, in an effort to understand a variety of different hybrid configurations and their potential to alter the energy production landscape.

Summary

The first two years of this project focused on systems making low-CO_2 load-following power and domestic synfuel. In FY 2012, the third year of this project, the depth of our analyses increased significantly. The emphasis of the applications was shifted somewhat to counter the variability of wind farm generation. From the technical aspects of the work, this was a matter of revising the assumed operating strategy.

The primary technical effort for this year was the development of a detailed, physics-based dynamic model of a representative hybrid energy system (see Figure 1). The system selected was based on a small modular light water reactor used to generate power to offset the variability of a wind farm's output. When not needed for this purpose, the nuclear plant's energy is diverted to a synfuel process that reformed natural gas to make syngas, which is then successively converted into methanol and from that gasoline. Although it is not specifically intended as the target of this work, the characteristics of the representative small modular reactor are those of the 500 MW (thermal) mPower pressurized water reactor from Babcock and Wilcox. This amount of nuclear energy input could produce either about 160 MWe of power or 35,000 barrels per day of gasoline and liquefied petroleum gas in each of two parallel trains.
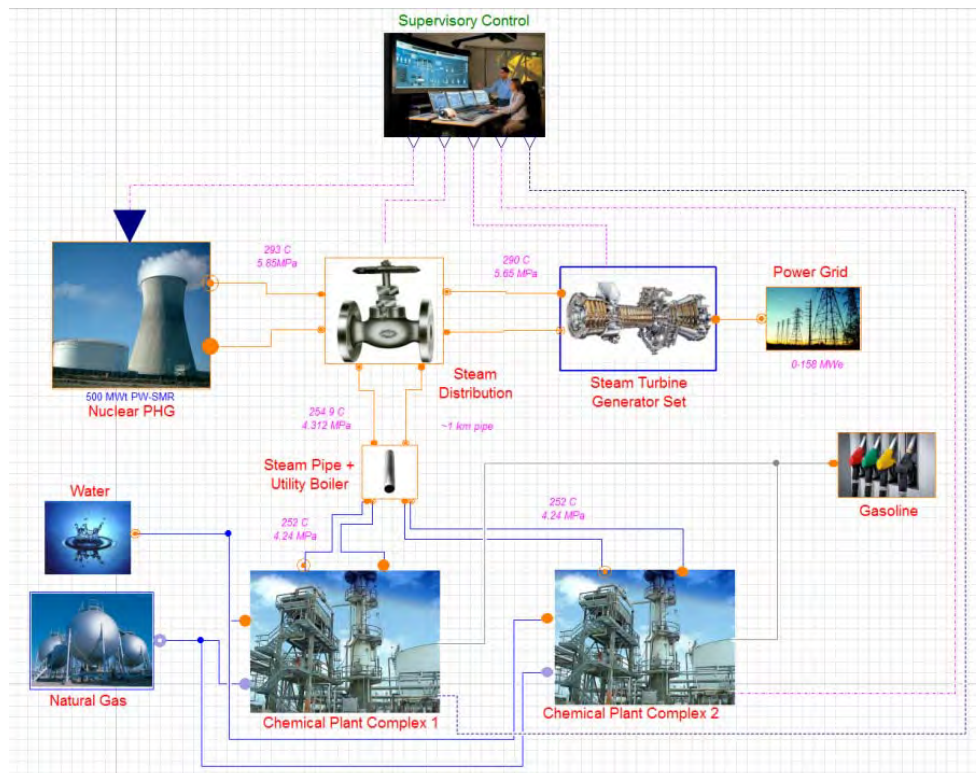
FIGURE 1. High level view of integrated HES Modelica-based model.

Programmatically, looking at the variability of wind farm generation was valuable in creating support for this effort among those supporting wind or solar power. In particular, program managers at the National Renewable Energy Laboratory (NREL) became interested in how nuclear hybrid systems could support their interests. In September 2011, INL was invited to present a talk sponsored by this project on nuclear hybrid systems at a conference at NREL on wind energy. As a result of those discussions, INL and the Joint Institute for Strategic Energy Analysis (a partnership of NREL and several energy companies and universities) co-hosted another R&D forum in May 2012 specifically devoted to identifying the research needed for nuclear HES to support increased renewable energy usage.

Also during FY 2012, INL was asked by the State of Wyoming legislature to examine whether nuclear HES could be used to help make value-added products from Wyoming's coal, natural gas, and wind resources. This CRADA work, funded by Wyoming, built directly upon this LDRD work by using methods and broad conclusions about desirable system configurations, in particular the value of methanol as a hybrid system product and precursor to other synthetic fuels and chemicals.

Benefits to DOE

In addition to improved economics, HES have two significant perceived benefits: (1) they can produce either electricity or synthetic fuels without emitting CO_2, and (2) they can produce vehicle fuels in the U.S. from U.S. resources, increasing the Nation's energy security. Both of these benefits—along with the obvious national benefits of less expensive electricity and fuel production—are key to DOE's mission of ensuring "America's security and prosperity by addressing its energy, environmental and nuclear challenges through transformative science and technology solutions."

Relevant Publications and Presentations

Aumeier, S.E., R. Cherry, R.D. Boardman, and J. Smith, "Nuclear Hybrid Energy Systems: Imperatives, Prospects and Challenges," *Energy Procedia*, Vol. 7, 51-54, 2012.

Cherry, R.S., S.E. Aumeier, and R.D. Boardman, "Large Hybrid Energy Systems for Making Low CO_2 Load-Following Power and Synthetic Fuel," *Energy Env. Sci.*, Vol. 5, 5489-5497, 2012.

Cherry, R.S. and R.D. Boardman, "Using Excess Electric Generation Capacity to Make Synthetic Fuels at the National Scale," in revision for Energy Policy, 2012.

Garcia, H., A. Mohanty, W-C. Lin, and R.S. Cherry, "Dynamic Analysis of Hybrid Energy Systems Under Flexible Operation and Variable Renewable Generation – Part I. Dynamic Performance Analysis," *International Journal of Energy*, 2012. (accepted)

Garcia, H., A. Mohanty, W-C. Lin, and R.S. Cherry, "Dynamic Analysis of Hybrid Energy Systems Under Flexible Operation and Variable Renewable Generation – Part II. Cost Analysis," *International Journal of Energy,* 2012. (accepted)

Carlsson, J., D. Shropshire, R.S. Cherry, A. Purvins, and I. Papaionescu, "Conceptual Evaluation of Hybrid Energy System Comprising Wind-Biomass-Nuclear Cogeneration For Load Balancing and Production of Low Carbon Electricity and Synthetic Transport Fuels," *Energy and Environmental Science*, 2012. (submitted)

Forsberg, C.W., Y.H. Lee, M. Kulhanek, and M.J. Driscoll, "Gigawatt-Year Nuclear-Geothermal Energy Storage for Light-Water and High-Temperature Reactors," *2012 International Congress on the Advances in Nuclear Power Plants, Chicago, IL, June 24-28, 2012.* (submitted)

Lee, Y.H., C.W. Forsberg, M. Driscoll, and B. Sapiie, "Options for Nuclear-Geothermal Gigawatt-Year Peak Electricity Storage Systems," *2010 International Congress on Advances in Nuclear Power Plants (ICAPP'10), San Diego, CA, June 13-17, 2010.*

Forsberg, C.W., R. Krentz-Wee, Y.H. Lee, and I.O. Oloyede, "Nuclear Energy for Simultaneous Low-Carbon Heavy-Oil Recovery and Gigawatt-Year Heat Storage for Peak Electricity Production," MIT-NES-TR-011, Massachusetts Institute of Technology, December 2010.

Lee, Y.H. and C.W. Forsberg, "Conceptual Design of Nuclear-Geothermal Energy Storage Systems for Variable Electricity Production," MIT-NES-TR-014, June 2011.

Forsberg, C.W., "Nuclear Energy for Variable Electricity and Liquid Fuels Production: Integrating Nuclear with Renewables, Fossil Fuels, and Biomass for a Low Carbon World," MIT-NES-TR-015, September 2011.

Development of Non-Lethal Methods for Enhanced Lipid Recovery from Microalgae

Deborah Newby, Brady Lee, and Lance Seefeldt[1]
10-078

Microalgae have displayed the potential for producing significant amounts of lipids for biodiesel. The DOE has identified dewatering as a significant technological and cost barrier to the feasibility of algal biofuels. Advanced and innovative dewatering systems are needed to increase efficiency and decrease costs. Development of physicochemical milking and molecular/systems biology approaches to understanding algal lipid metabolism and excretion are key deliverables designed to establish a foundation for follow-on work. The integrated molecular analyses conducted on *Chaetoceros gracilis* will provide key insights into lipid production and trafficking, which are essential to understanding algae as a feedstock, will help in the development of non-lethal milking approaches, and may ultimately facilitate genetic engineering of this and other microalgae strains. This LDRD project was designed to serve as the nucleation point to add an algal component to INL's renewable energy/alternative fuels portfolio. The end objective of this work is to have gained fundamental understanding of lipid production, metabolism, and excretion/extraction in order to help drive technology decisions that will improve the economic feasibility of production and recovery of lipids from microalgae.

Summary

This project served as a nucleation point for the INL algal biofuels program. During execution of this work we have developed in-house expertise in the growth and maintenance of a variety of high lipid producing algal strains, understanding of lipid development within algal cells, and in analytical techniques for lipid analysis including fluorescence staining (Figure 1) and gas chromatography/flame ionization detection (GC-FID).
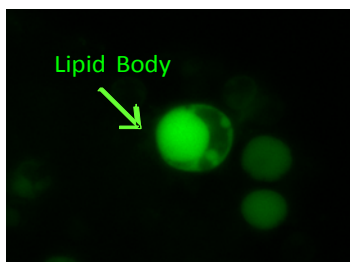
FIGURE 1. *Chlorella* cell stained with Nile Red, showing lipid content (Day 10).

A variety of shock (e.g., salt, temperature, light) and biocompatible solvents (>10) were assessed to determine their ability to non-lethally remove lipids A two-phase system to recover lipids from actively growing algal cultures using biocompatible solvents was developed and shows promise for lipid recovery while maintaining cell viability. Lipid extracted from *Chaetoceros gracilis*, a high lipid producing diatom, using a biocompatible solvent system is depicted in Figure 2. The general premise for this work led to the submission of nine invention disclosure records for a similar system, using a novel solvent system that warrants further exploration. Continued funding for this work is being sought from a CRADA partner.
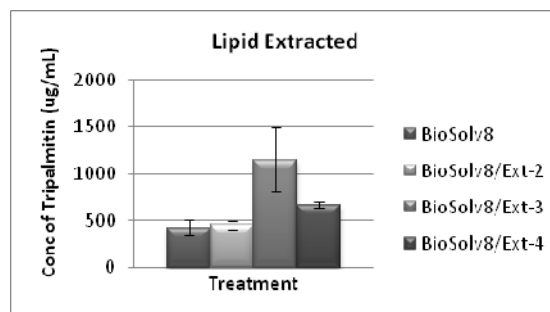
FIGURE 2. Quantity of a representative lipid (tripalmitin) extracted from C. gracilis with sonication and GC-FID analysis.

To gain molecular-based insight into lipid production and trafficking, DNA from a culture enriched for *Chaetoceros gracilis* (and bacteria that grow in close association) were isolated and sequenced. Analysis of this metagenomic information required development of a bioinformatic pipeline to identify and annotate algal and bacterial sequences from the consortium. This bioinformatics infrastructure is a valuable new capability for all biological research projects at INL and collaborating institutions. Over 41,000 protein coding genes were identified in the scaffolds of 45,000,000 basepairs. Sequences for genes of interest, including hundreds involved in algal lipid synthesis pathways, were identified, and probes for microarray analysis designed to facilitate monitoring of temporal gene expression during growth. Probes representing approximately 44,000 algal gene sequences were designed and 12 high density microarrays were fabricated using these probes.

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[1] Utah State University

An intermediate-scale time course study using four "mini" ponds configured using 100 L clear containers filled with approximately 50 L of culture and illuminated grow light panels to regulate a light/dark cycle for algal growth was inoculated with *C. gracilis*. Samples were collected at four time points representing lag, log, and stationary phases of growth. RNA was extracted and converted to cDNA for microarray analyses. Lipid samples were shipped to collaborators at Utah State for analysis. Carbohydrate, optical density, nitrogen, and phosphate were also monitored throughout the growing cycle. The fabricated microarrays were then used to determine differences in gene expression during different phases of growth, as well as under different nutrient regimes, specifically related to decreases in nitrogen and phosphorus due to depletion of the medium during cell growth. Microarray design, fabrication, and data generation was performed through a subcontract with Roche Nimblegen. Labeled cDNA from each time point was then hybridized to the microarray and probe response from each microarray was analyzed. Data generated from the microarray experiments is currently being analyzed. This metagenomic information enables genetic and expression analysis of *C. gracilis* and is a significant contribution to the algal biofuels field as only a limited number of algae gene expression studies have been conducted.

The work and tools developed through this initial algal LDRD served as the nucleation point for two projects focused on algae feedstock logistics and algal dewatering. Metagenomic information gained from this work formed the foundation of an independent LDRD that was initiated in FY 2012, "Designing Algal Biofuel Consortia for Increased Function and Reduced Nutrient Cost." This work was also the foundation for a CRADA that addresses removing barriers to algal biofuel production. In addition, it helped establish key partnerships with Pacific Northwest National Laboratory, National Alliance for Advanced Biofuels and Bio-Products (a large DOE algae consortium), Utah State University, Boise State University, and the University of Idaho. In addition, work conducted here has been leveraged by projects funded through the CAES and use of the microarray developed here is being explored in concert with some of that work. We continue to build strong regional and national laboratory partners in the algal biofuels arena.

Benefits to DOE

Algae have great promise as a platform for economical, domestic, low-carbon, low land-impact, and low-water impact liquid biofuel. However, to be viable in the energy marketplace, algae will need to be grown in open air pools, a major challenge to realizing theoretical yields and economics. By increasing our understanding of biofuel-relevant algae and their natural consortia, we aim to enable the DOE's mission to secure a sustainable energy future. In addition, the data we have collected may support missions involving water (both related to remediation and to toxic algal blooms) and CO_2 capture in algal dominated ecosystems.

Relevant Publications and Presentations

Henriksen, J.R., B.D. Lee, and D.T. Newby, "*Chaetoceros Gracilis* Dominated Metagenome Reveals Genetic Potential of an Algal Biofuel System," 2013. (in preparation)

Newby, D.T., D. Stevens, B.D. Lee, and K. Schaller, "Metagenomic Analysis: from Reading DNA to Environmental Understanding," *The Second Annual CAES Workshop on Modeling, Simulation and Visualization*, *Boise, ID, September 9, 2011*.

Newby, D.T., B.D. Lee, J. Henriksen, J. Ellis, and R. Simmons, "Targeted Genomic Analysis of *Chaetoceros Gracilis*," *Algae Biomass Summit of the Algal Biomass Organization, Minneapolis, MN, October 25–27, 2011.*

Biological Fixation of CO₂ for Fuel and Chemical Production Using Acetogen Intermediary Metabolism

William Apel, Brady Lee, and John Aston
10-087

Acetogenic bacteria possess flexible metabolisms allowing the use of many different substrates for catabolic and anabolic processes, most of which involve the generation of Acetyl-coenzyme A (CoA), which is a versatile intermediate metabolite that may serve as a precursor for the synthesis of different biomolecules, or may be oxidized for energy, a process that produces acetate. Other potential compounds produced by acetogens are pyruvate, butyrate, propionate, formate, syngases, ethanol, and butanol. As such, they are excellent targets for development of a biological system that can be optimized for the conversion of atmospheric CO_2 into value-added products. This LDRD project explored the potential of carbon fixation genes related to the acetyl-CoA biological pathway in several acidic and alkaline hotsprings in Yellowstone National Park (YNP) and Oregon's Alvord Desert (AD) using metagenomic sequencing and analysis. In addition, this project sought to isolate acetogenic microorganisms from these environments, and characterize and optimize the CO_2 fixation by the known thermophilic acetogen, *Moorella thermoacetica*.

Summary

Metagenomic data from five hot springs in YNP were obtained through a joint collaboration with the Thermal Biology Institute at Montana State University. In addition, metagenomic data from AD hot springs and two additional YNP hot springs were made available through sampling efforts within this project. These sequence data were trimmed and assembled into meaningful genetic data. This data has been assembled into a unique database, against which known enzymes related to the Acetyl-CoA pathway may be compared. This information may be later used to identify enzymes and genes of commercial interest and inform future research with respect to geochemical and environmental controls on the biological fixation of CO_2. In addition to surveying the metagenomic potential of these hotsprings, environmental samples were collected from three hot springs from the AD and four hot springs from the Norris Geyser Basin in YNP. The temperatures of these environments range from 40–80°C, and the pHs vary between 3.5 and 9.0. Aliquots from these samples have been enriched under acetogenic conditions, and metabolomic analyses have shown a shift towards acetate and ethanol production correlated with CO_2 and H_2
consumption. Isolation efforts have yielded one species, which may be characterized in future work.

In parallel to characterizing the biological potential for the conversion of CO_2 to value-added chemicals through the acetyl-CoA pathway, research within this LDRD examined methods to optimize such a process using the previously studied thermophilic acetogen, *M. thermoacetica*. Specifically, a metabolic modeling method that predicts and optimizes the flow of energy and material through microbial systems was been constructed from the annotated genome of *M. thermoacetica*. The output data from this model can be sorted against various cellular strategies, such as maximal efficiency of biomass yield per substrate, and substrate consumption in the presence of high exogenous concentrations. Output from such model analysis successfully predicted substrate concentrations that maximize ethanol production, as opposed to acetate, when *M. thermoacetica* was grown on CO_2 and H_2. In fact, the molar ratio of produced ethanol:acetate increased 80-fold when substrate conditions were adjusted per the models predictions (Figure 1).
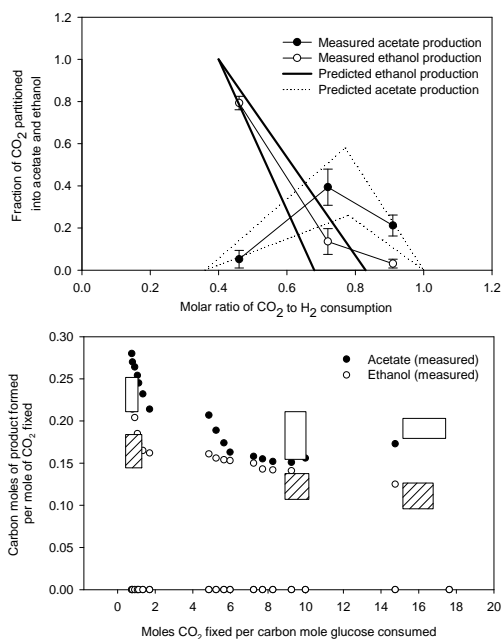
FIGURE 1. Comparison of measured and model predicted acetate and ethanol production by *Moorella thermoacetica* grown on CO_2 and H_2 (top) and CO_2, H_2, and glucose (bottom).

In addition, *M. thermoacetica* was grown using direct current as the sole electron donor, and as with H_2 supported growth, we observed an apparent functionality between the electron donor/acceptor availability and metabolite production (Figure 2). Additional data, not shown, indicated the functionality between both CO_2 partial pressures and direct current loading with the partitioning of carbon to either acetate or ethanol. These exciting results suggest that *M. thermoacetica* can produce value-added chemicals using excess electrical energy and CO_2.
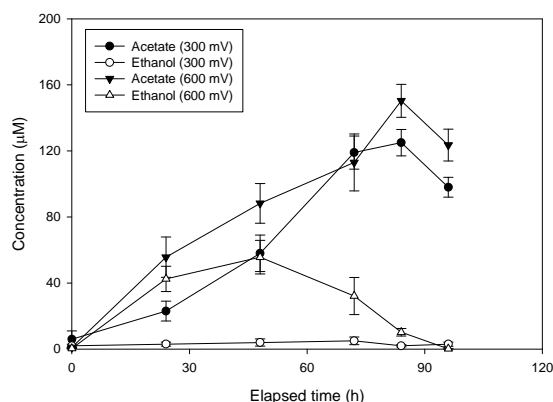
FIGURE 2. Production of acetate and ethanol by *Moorella thermoacetica* grown on CO_2 and direct current at both 300 and 600 mV.

Benefits to DOE

This project supports the missions of both DOE's Office of Energy Environment and Renewable Energy and Office of Science by developing the technology basis for a renewable process to produce value-added fuels and chemicals while decreasing atmospheric carbon dioxide concentrations.

Relevant Publications and Presentations

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Application of Metabolic Flux Modeling to Predict Carbon Flow and Metabolite Production by the Model *Acetogen Moorella Thermoacetica*," 2012. (in preparation)

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Metabolic Model Informed Adjustment of CO_2 and H_2 Tensions to Optimize Ethanol Production During Chemostat Culturing of the Thermophilic Acetogen *Moorella Thermoacetica*," 2012. (in preparation)

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Production of Acetate and Ethanol Using Direct Current and CO_2 by the *Moorella Thermoacetica*," 2012. (in preparation)

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Effects of Exogenous Concentrations of Organic Acids and Alcohols on the Growth and Acetate Production of the Acetogen *Moorella Thermoacetica*," 2012. (in preparation)

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Using Metabolic Flux Models to Optimize the Biological Production of Value-Added Chemicals from CO_2," *Society for Industrial Microbiology and Biotechnology Meeting, Washington, D.C., August 2012*. (invited)

Aston, J.E., B.D. Lee, H. Lee, and W.A. Apel, "Metabolic Flux Analysis of an Acetogen Metabolism: *Moorella Thermoacetica*," *11th International Conference on Thermophiles Research, Big Sky, MT, September 2011*.

Jaeger A., L. Taylor, R. McIsaac, A. Torres, J.E. Aston, A. Staven, M.H. Lee, B.D. Lee, and W.A. Apel, "Molecular Methods to Access Thermophilic Acetogenic Enrichment Cultures," *Idaho National Laboratory, Student Research Expo, Idaho Falls, ID, August 2010*.

Hybrid Osmosis Water Purification Systems Research

Frederick Stewart, Mark Stone, and Aaron Wilson

10-092

The availability of fresh water for both domestic and agricultural use is becoming a significant challenge in parts of the U.S., leading to conflicts over priorities. Furthermore, increased development of domestic hydrocarbon resources has placed more stress on available water supplies and created a need for inexpensive treatment options. Forward osmosis (FO) is a rapidly evolving novel water purification technology that offers the inherent promise of low cost water processing by using naturally occurring osmotic pressure gradients to selectively transport water across a semi-permeable membrane.

To increase the market acceptance of FO, two technical challenges exist: membranes and draw solutions. FO membranes typically consist of porous polymeric materials adapted from mature reverse osmosis processes. Reverse osmosis employs energetically expensive mechanical pressure to overcome osmotic gradients to transport water from a contaminated feed to a clean stream. Reverse osmosis membranes employed in FO operate by providing channels for water passage and they currently are available from several commercial vendors. Further, many institutions are dedicating significant efforts to the development of novel FO membranes. The second enabling aspect of an FO process is the draw solution. For FO to function, an engineered draw solution with high osmotic potential—greater than that of the selected feed—is required. Another requirement is the ability to economically strip the water from the draw solution in a second step. Under this scenario, water transports across the membrane and into the draw solution without the need of energy input. However, reclaiming the water from the draw requires some energy input.

The goal of any engineered draw solution system is to facilitate water separation with a minimum of inputted energy. Engineered draw solutions that obtain high flux rates from challenging feeds (such as produced and saline waters) and are easily stripped of transported water need to be developed. Thus, this project focused on developing new draw solution chemistries, demonstrating both FO and second stage water removal on the laboratory scale, and determining the critical parameters necessary for development of a deployable process. Further, the project team sought to develop a network of academic and industrial collaborators that can use novel INL technology to enable a water purification system based on FO.

Summary

Two new draw solution processes were developed in this project. First, a hexavalent cyclotriphosphazene salt was synthesized and demonstrated in an FO first stage, followed by second stage nanofiltration to re-concentrate the salt for reuse in FO. The phosphazene salt was developed because of its high water solubility and osmotic potential, and also because of its molecular size, which made it easier to separate from water. Experiments showed that the phosphazenes maintained high osmotic pressures and exhibited no significant back-diffusion, which is common to smaller inorganic salts, and could also be readily re-concentrated by nanofiltration.

As a second process, switchable polarity solvents (SPS) were demonstrated to be viable draw solutes. SPS is an organic that can switch between polar and non-polar forms with a controllable stimulus, such as the presence of CO_2. In particular, tertiary amines were found to be non-polar in the absence of added CO_2. However, with CO_2, they form highly water-soluble solutes that achieve considerable osmotic potential, as shown through both laboratory-scale FO experiments and through freezing point osmometry. To further demonstrate the SPS concept, FO experiments were conducted against both saline feeds of varying concentrations (up to 5 molal NaCl) and simulated produced water feeds, which include both organic and inorganic components at relatively high concentrations. The saline water experiments were particularly exciting because commercially attractive water flux rates were obtained up to 5 m concentration, which is approximately 10 times the concentration of sea water.

An FO process has been proposed using the SPS concept, see Figure 1. This process includes both an FO stage and a thermal stage for driving off CO_2 using a low grade heat source, which causes the SPS to phase separate from the water facilitating mechanical separation of purified water. Also included is a final polishing step, if needed. Economic analyses performed by INL and Hydration Technologies Innovations, Inc.—the company that has signed a license option agreement for the technology—have determined that the SPS concept is a commercially viable FO process.
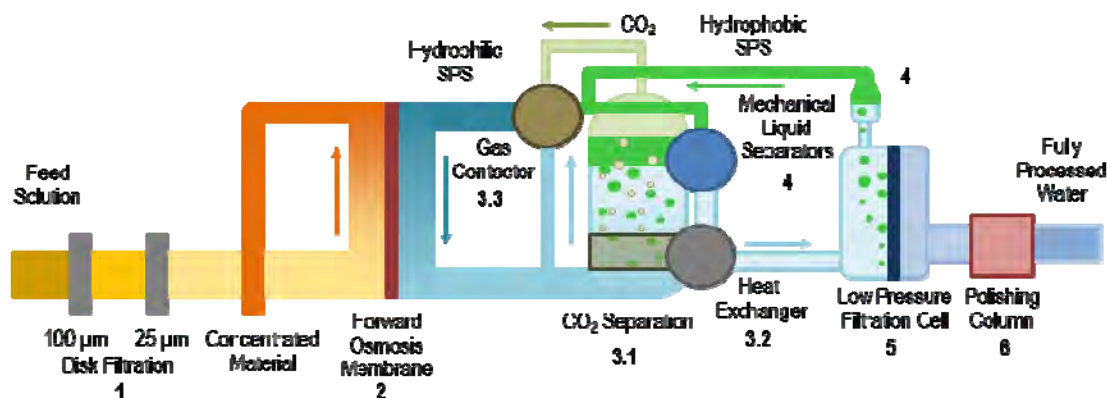
FIGURE 1. SPS FO process diagram.

U.S. Patent applications have been filed that discuss the two new draw solute technologies. In response to this technology, INL has signed non-disclosure agreements with three companies who manufacture FO membranes and systems and at least two have discussed licensing these new technologies. This project also was used to develop collaborations with academic research groups to provide aspects of the overall process that INL is lacking, including new membrane design (University of Connecticut) and process scale-up facilities (Colorado School of Mines).

Benefits to DOE

DOE is tasked with safeguarding energy security, which is known to be inextricably linked to water security. Water security addresses supply concerns and this project directly addresses the utilization and recycle of water. The new water purification capability developed in this project is designed to address and solve nationally significant problems in water treatment and reuse, which may have applicability in domestic, industrial, and agricultural settings.

Relevant Publications and Presentations

Two patent applications have been filed as follows:

Stone, M.L., F.F. Stewart, and A.D. Wilson, "Methods and Systems for Treating Liquids Using Switchable Solvents," U.S. Patent Application 13/480,053.

Stewart, F.F., M.T. Benson, and M.L. Stone, "Water Purification by Synthesis and Operation of a Forward Osmosis Draw Solute," U.S. Patent Application 13/479,726.

Stone, M.L., C. Rae, F.F. Stewart, and A.D. Wilson, "Switchable Polarity Solvents as Draw Solutes for Forward Osmosis," *Desalination*, 2012.

Stone, M.L., A.D. Wilson, M.K. Harrup, and F.F. Stewart, "An Initial Study of Hexavalent Phosphazene Salts as Draw Solutes in Forward Osmosis," *Desalination*, 2012. (submitted)

Integration of Renewable Energy Resources Through Energy Storage and SuperGrid

Thomas Baldwin and Mike West
11-007

In 2012, the Assistant Secretary for DOE-Energy Efficiency & Renewable Energy (EERE), Dr. David Danielson, challenged the renewable energy programs with reaching 80% renewable energy penetration by the year 2050. As part of this challenge, 40% of generation would be of the variable power type, such as wind and solar. The technical problem can be simplified in its description to one of integration of different types of generation onto an unforgiving electrical grid. A few key research questions spring from this challenge: (1) what is the optimal way of adding variable generation to the grid, (2) how can energy storage and hybrid energy systems (including nuclear energy resources) smooth the power and energy fluctuations for a stable electric grid, and (3) how should the grid evolve to accommodate renewables and hybrid energy generation, energy storage, and new electrical loads such as electric vehicles. The constraints for the challenge include achieving secure, reliable, and resilient energy delivery.

The project aims to: (1) develop the modeling and analysis tools to understand the interfacing issues of renewable energy generation to the electrical power grid, (2) determine the impact of placing large-scale energy storage in the power grid to support integration of renewable energy generation, and (3) determine the impact of operating a super-grid on the penetration of renewable energy generation. The LDRD begins with tools and model development, leading to analysis and the development of best engineering practices. At the end of the LDRD, the conceptual plans for a follow on demonstration project will be developed.

The developed computational tools characterize the dynamic interactions of grid systems where energy storage is used to stabilize the grid. The computational tools support the engineering expertise to analyze and integrate renewable and hybrid energy systems to the electrical grid. The LDRD builds upon the capabilities of INL to address electrical power storage where electrical power may not always be dispatchable and where grid stability and reliability depends on managed load following and supply.

We are identifying and studying process and grid controls, transmission solutions, and energy storage solutions necessary to couple mixtures of small base-loading constant energy and mid-loading non-dispatchable (variable or intermittent) energy resources to the electric power grid. Three groups of technical solutions being considered from the electrical perspective to develop control strategies and identify the optimal size and grid location for large-scale energy-storage systems (on the order of 100 MWh or 3.6×10^{11} J and larger) for short-term storage (approximately 15 minutes) to address power imbalances and grid instability due to variable or intermittent generation. The work focuses on the electric grid in terms of system performance and the technical challenges with the goal of achieving higher levels of reliability and efficiency in grid performance. The specific focus is on wind and solar energy, the renewable resources with the most potential for significant penetration. Milestones of this effort include: (1) acquiring or developing the analysis tools to evaluate electric grid control and power plant process control schemes, (2) developing models of grid components and power plants for evaluating and validating new schemes, and (3) identifying best engineering practices for control philosophies and energy storage sizing, placement, and operating schemes.

Summary

In the first year, a number of energy storage technologies were evaluated on the bases of engineering sizes and capabilities as well as costs and implementation readiness. Key results indicated that many energy storage technologies work well at small scales (<1 MJ) and for niche applications. Electric grid applications stress these technologies as energy storage requirements fall into the gigajoule and terajoule (1 MWhr to 1 GWHr) range. Technologies that are viable today at these scales are pump-hydroelectric, compressed air, and battery bank systems. Energy density and power density issues remain problematic from many storage technologies. Capital costs for energy systems are also higher than the electricity market is willing to pay.

The characteristics of variable generation were studied. A key aspect is the stochastic nature of power from wind and solar production. The understanding of the probabilities of supplying power from renewables is necessary for grid integration. The risk of not producing sufficient power is mitigated by expanding the grid control area that supports with spinning reserves. Increasing the penetration of renewables complicates the risk of not producing sufficient power. The concept and quantification of statistical independence of wind and solar resources influences the results of spatial and temporal diversity of renewable resources.

In the second year, the integration of generic variable generation into a simplified grid has been studied. Energy storage systems were introduced near the generation and load centers. We assessed the costs and benefits of energy storage. Energy storage demonstrated two important functions: storage near variable generation can be applied to smooth the energy output to match the electric grid's ability to absorb the power; and energy spillage can be mitigated by sizing the storage capacity. Forced power ramping of conventional thermal power plants due to renewable energy can be reduced with the application of energy storage. A sensitivity analysis has been performed to understand the impact of various levels of renewable penetration into the grid.

Benefits to DOE

The DOE Offices of EERE and Electricity Delivery and Energy Reliability (OE) have established a set of mission objectives through the collaborative Grid Tech Team. These objectives have been expressed as a roadmap for the 2030 Grid. Key aspects include:

- Developing the Grid 2030 architecture
- Developing and demonstrating critical technologies such as energy storage and smart controls
- Accelerating the acceptance of new technologies
- Strengthening the energy market operations
- Building government-education-industrial partnerships.

This effort supports the ongoing R&D work of integrating renewable and hybrid energy resources by providing engineering tools and architectural solutions for the electric power grid. The results of this work are fundamental to the future operation of electric power systems where CO_2 emissions must be regulated and electric vehicles are commonplace. Energy security, reliability, and resiliency will be key characteristics of the new grid. Other outcomes of the project include the buildup of capabilities and expertise in electric power engineering research that supports activities in small-modular nuclear, biomass, geothermal, hydro, and wind energy systems.

As the electric power industry is required to move towards greener energy sources and implement a Smart Grid for the benefit of customers, many future technical barriers must be addressed. This work prepares INL with technical expertise and tools to conduct the needed research. It is expected that significant investments in research and development are needed and will be funded by utilities, emerging suppliers of green energy generation, and such organizations as Electric Power Research Institute.

Relevant Publications and Presentations

West, M. and T. Baldwin, "Energy Storage and SuperGrid Integration," *2013 North American Power Symposium, Manhattan, KS, September 2013.* (submitted)

Electrochemical Production of Synthesis Gas from CO$_2$

Tedd Lister and Eric Dufek
11-019

Electrochemical reduction of CO$_2$ is a technology that could integrate intermittent alternative energy sources into the electric grid by using excess energy to create a storable energy product. Electrochemical reduction of CO$_2$ has been demonstrated for many years and is capable of generating high product yields of reduced carbon species using moderate conditions. This project involves developing the technology for electrochemical reduction of CO$_2$ to synthesis gas (syngas). We believe this can serve as a source of reduced carbon feedstock for follow-on synthetic pathways to commodity chemicals. This project is focused on developing systems reported in laboratory-scale studies into working bench-scale, and eventually pilot-scale, processes.

Syngas is a very useful mixture of H$_2$ and CO that can be used to synthesize a variety of commodity chemicals and transportation fuels using established methods. Conventional syngas production methods use fossil resources that release carbon into the atmosphere. Electrochemistry offers a clean method of producing syngas. Thus, this process could be configured to act as load leveling devices for intermittent electrical supplies and converting this energy to a useful product. The challenge for this work is to perform the electrolysis with the minimum energy input and produce a useful product stream at high throughput.

Summary

The project achieved its primary goals—culminating with the demonstration of a pressurized system for electrolysis of CO$_2$. This system demonstrated high current densities while maintaining high selectivity for CO production. The project has produced four peer-reviewed papers (a fifth is in review) and four presentations at conferences and workshops. In addition, a process for coupling syngas production with chlorine gas production (chlor-syngas) has been developed. Another idea that has sprung from this project involves using a high pressure electrolysis system to electrochemically upgrade pyrolysis oils. This project is awaiting external funding from the DOE Biomass Program (full proposal has been submitted). Other opportunities for external funding have been pursued including a full proposal to DOE's Energy Efficiency & Renewable Energy Advanced Manufacturing Funding Opportunity Announcement (FOA) and concept paper to the FY 2012 Advanced Research Projects Agency-Energy (ARPA-E) FOA. Our partner, Giner Inc., has obtained Small Business Innovation Research (SBIR) Phase 1 funding from the U.S. Air Force to pursue syngas generation for synthetic fuel production. Giner also plans to submit an SBIR proposal to DOE for the choro-syngas concept.

Benefits to DOE

This project fits into a larger effort to develop technologies that use low value energy to transform CO$_2$ into hydrocarbon products. In addition, this project addresses issues of integrating the vast renewable energy resources of the Western Inland Energy Corridor, which possesses many natural energy resources but has limited grid connections to transport electricity to larger population areas. Generation of hydrocarbon-based fuels during periods of low cost power could act as a load level during periods of high power output or low customer usage. Thus this project could be a part of a group of technologies to reduce U.S. dependence on foreign oil imports, increasing America's energy security, which is a major part of DOE's mission. Early results have been presented at an international conference and a paper describing novel results is in preparation.

The project has developed a permanent hire at INL who has performed much of the experimental work for this LDRD project.

Relevant Publications and Presentations

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Bench-Scale Electrochemical System for Generation of CO and Syn-Gas," *Journal of Applied Electrochemistry*, Vol. 41, 623, 2011.

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Influence of S Contamination on CO$_2$ Reduction at Ag Electrodes," *J. Electrochem Soc*, Vol. 158, B1384, 2011.

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Influence of Electrolyte and Membranes on Cell Operation for Syn-Gas Production," *Electrochemical and Solid State Letters*, Vol. 15, B48, 2012.

Dufek, E.J., T.E. Lister, S.G. Stone (Giner, Inc.), and M.E. McIlwain, "Operation of a Pressurized System for Continuous Reduction of CO_2," *Journal of Electrochemical Society,* Vol. 159, F514, 2012.

Lister, T.E., E.J. Dufek, and M.E. McIlwain, "Chlor-syngas: Coupling of Electrochemical Technologies for Production of Commodity Chemicals," Energy and Environment. (submitted)

Dufek, E.J., T.E. Lister, and M.E. McIlwain," Bench-Scale System for Electrochemical Reduction of CO_2," *Future Direction in CO_2 Conversion Chemistry Workshop, Princeton University, Princeton, NJ, October 31, 2010.*

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Investigation of CO_2-H_2O Reduction Scale-up: Production of Syn-Gas Mixtures," *Electrochemical Energy Summit, 220th Electrochemical Society Meeting, Boston, MA, October 9–11, 2011.*

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Implications Associated with S Contamination for the Production of Syn-Gas from CO_2 Reduction," *Electrochemical Society Meeting, Boston, MA, October 11, 2011.*

Dufek, E.J., T.E. Lister, and M.E. McIlwain, "Bench-Scale Electrochemical Production of Synthesis Gas," *2012 AIChE National Meeting, Pittsburgh, PA, October 28–November 2, 2012.*

Mechanisms of Self Inhibition of Catalytic Conversion of CO_2 to Methanol

Daniel Ginosar, Lucia Petkovic, Rao Kondamudi, and Nicholas McGuire
11-031

The ability to convert significant quantities of carbon dioxide (CO_2) directly to fuels is limited by CO_2 self inhibition on catalyst kinetics. To realize the capability of the carbon-to-chemicals program, new catalysts need to be developed that are not inhibited by high concentrations of CO_2. The significance of this research project is to develop the theory that identifies the nanoscale morphology/self inhibition of CO_2 on fuel production and to use this theory to enable a significant increase in CO_2 conversion to fuels.

Summary

The characterization and performance of lanthanide-promoted zirconia catalysts for synthesis of isobutene from syngas (isosynthesis) was investigated. Several mixed metal-oxide catalysts employing a range of modifier species were considered. The catalysts examined include lanthana-promoted zirconia, ceria-promoted zirconia, and lanthana-ceria zirconia. The addition of metal promoters to zirconia is known to have an effect on the physicochemical properties of the catalyst which in turn affects catalytic performance for isosynthesis. Pure zirconia, ceria-zirconia, lanthana-zirconia, and ceria-lanthana-zirconia isosynthesis catalysts were prepared using the method of surfactant-assisted coprecipitation. This method was originally developed for synthesizing high-surface-area zirconia catalysts that are effective for n-butane isomerization. Incorporation of metal promoters (i.e., lanthana and ceria) was achieved by adding an appropriate nitrate to the initial zirconyl chloride mixture. All catalyst powders tested were pelletized, crushed with mortar and pestle, and sieved to a 40-60 mesh size prior to reaction testing or characterization.

Catalyst properties were characterized via a number of diagnostic techniques including N_2 physisorption, x-ray diffraction, and diffuse reflectance infrared Fourier transform (DRIFT) analysis following probe-molecule chemisorption. X-ray diffraction (XRD) is used to characterize the relative crystallinity, crystallite size, and phase of the zirconia-based isosynthesis catalysts. XRD spectra for the pure zirconia catalysts show that the majority of the crystal structure is in the tetragonal phase. Additional diffraction peaks indicate that a small percentage of the monoclinic phase is present. Similarly, the zirconia-based catalysts incorporating ceria show that a large percentage of the crystal structure is in the tetragonal phase of zirconia. In contrast to the ceria-promoted sample, incorporation of lanthana as a promoter into the zirconia crystal structure results in a larger percentage of the crystal structure being in the tetragonal phase. In addition, the lanthana-promoted zirconia samples show relatively wide diffraction peaks in the XRD pattern. Such wide peaks indicate that zirconia-based catalysts incorporating lanthana have smaller crystallite sizes relative to the pure zirconia catalysts or ceria-promoted catalysts.

The pure zirconia catalyst has a surface area of approximately 147 m^2g^{-1} and a total pore volume of 0.27 cc g^{-1}. The addition of the lanthanide promoters (lanthana and ceria) has observable effects on the physical characteristics of the zirconia catalyst. The incorporation of lanthana reduces the overall surface area by 29% to 105 m^2g^{-1} and the average pore volume to 0.21 cc g^{-1}. The addition of ceria has similar effects. The overall surface area and total pore volume are reduced by 32% and 30%, respectively. Adding both promoters to the zirconia catalysts has a similar effect still. The zirconia-based sample with a mix of ceria and lanthana heteroatoms has physical characteristics similar to that of the binary compounds.

The pore-size-distribution for the pure zirconia showed two peaks indicating a bimodal distribution of pore sizes. The larger pore sizes in the distribution average close to 10 nm while the smaller peak in the pure zirconia catalyst pore size distribution indicates pore sizes of about 2 nm. The peak indicating a distribution of smaller pore sizes is not observable in the pore size distribution for the lanthanide promoters suggesting that the addition of promoters eliminates smaller pore sizes. Furthermore, when zirconia samples include lanthana promoters the average pore size is shifted to slightly higher values when compared to the pore sizes of the pure zirconia sample.

Pyridine adsorption studied by DRIFTS analysis reveals the relative acidity of the mixed metal oxide isosynthesis catalysts. The pure zirconia sample is the most acidic of all the samples tested in this work. Several absorbance peaks are present after N_2 purging of the zirconia sample. This indicates Lewis acid sites, Bronsted acid sites, and a combination of Bronsted and Lewis acid sites.

The zirconia sample promoted with ceria has similar DRIFTS absorbance peaks in comparison to the pure zirconia sample. The absorbance peaks due to pyridine adsorption of the ceria promoted sample are observed at a reduced intensity relative to the pure zirconia sample indicating that there are fewer numbers of acidic sites overall. The zirconia samples incorporating lanthana show the lowest acidity of all the samples tested. The intensities for all chemisorbed peaks are reduced significantly relative to the pure zirconia sample. The three part mixed metal oxide, lanthana-ceria-zirconia samples showed similarly reduced intensities for Bronsted and Lewis acid sites. However, in contrast to the lanthana-promoted sample the primary acid sites observed here are of the Bronsted type. Similar to the ceria-promoted samples the overall number of acidic sites for this sample is also reduced relative to the pure zirconia sample.

Isosynthesis activity was evaluated in a packed bed reactor configuration and the results were analyzed in terms of the physicochemical characteristics of the catalysts. Catalyst activity test results indicate that the species of the modifier has a strong effect on carbon monoxide conversion and selectivity to isobutene. The pure zirconia converts approximately 14% of the input carbon monoxide at 10 h on stream. Of the carbon monoxide converted, the C_4 yield is 15% and the CO_2 yield is 35%. Alcohols were not detected in any appreciable amount for the pure zirconia sample. Isobutene yield is approximately 9% of the converted CO. The addition of metal oxide promoters has significant effects on the isosynthesis activity of the zirconia catalyst. Most notably, the carbon monoxide conversion is reduced by about 50% to levels between 5 and 7% at 10 h on stream. This reduction is consistent regardless of the promoter species. The species of the promoter also has different effects on the selectivity of the catalyst. Adding lanthana reduced the selectivity to isobutene to approximately 5%. In contrast, adding ceria does not significantly affect the selectivity to isobutene. The zirconia catalysts with the ceria promoter have similar selectivity to hydrocarbons relative to the pure zirconia sample. The sample that is a three part mixed metal oxide shows carbon monoxide conversion levels and selectivity to isobutene on the same order as the zirconia catalyst promoted with lanthana. In addition, when considering the selectivity to isobutene in total C4 products, the highest isobutene selectivity was displayed by the sample without promoters. The lowest was displayed by the two samples containing lanthanum.

Research efforts then focused on the effect of CO_2 on the conversion of synthesis gas to iso-alkenes via the isosynthesis reaction. In general, between 1 and 2% CO_2 in the synthesis gas increased product yields while higher concentrations depressed yields. Surprisingly, low molecular weight iso-alkenes were not the major product. Instead, it was discovered that hydrocarbons in the jet fuel molecular weight range were the predominate product. This discovery led to an invention disclosure record and a funds-in CRADA.

Benefits to DOE

The discovery of the jet fuel molecular weight compound production from synthesis gas will enable the U.S. to be more energy independent. Domestic products such as biomass, waste, natural gas, and coal can all be gasified to synthesis gas and then converted to jet fuel over the catalyst discovered in this project. In addition to meeting DOE goals, the production of jet fuel from domestic products will be beneficial for DOD needs.

Relevant Publications and Presentations

Petkovic, L.M. and D.M. Ginosar, "Synthesis of Isobutene and Isobutane from Synthesis Gas. A Literature Review Since 1992," *Current Catalysis*, Vol. 1, 52–57, 2012.

McGuire, N.E., N. Kondamudi, L.M. Petkovic, and D.M. Ginosar, "Effect of Lanthanide Promoters on Zirconia-Based Isosynthesis Catalysts Prepared by Surfactant-Assisted Coprecipitation," *Applied Catalysis A-General*, Vol. 429, 59-66, 2012.

McGuire, N.E., N. Kondamudi, L.M. Petkovic, and D.M. Ginosar, "Effect of Modifiers on Zirconia-Based Catalysts for Isosynthesis," *American Institute of Chemical Engineers Annual Meeting, Minneapolis, MN, October 16–21, 2011.*

Ginosar, D.M. and L.M. Petkovic, "Effect of Carbon Dioxide on Zirconia-Based Catalysts for Isosynthesis," *2012 Idaho Academy of Science Symposium, Idaho Falls, ID, March 23, 2012.*

Multiscale Coupled Hydrogeophysics Modeling: Advancing Understanding of Reactive Transport and Effective Subsurface Environmental Monitoring

Hai Huang, Chuan Lu, and Tim Johnson[1]

11-045

We are developing coupled hydrogeophysics models to provide more effective and more reliable subsurface monitoring techniques for a number of subsurface applications, including three-dimensional (3-D) spatial-temporal mappings of contaminant plumes in the subsurface, hydraulic fracture propagations, and fluid leakage associated with recovery of oil and gas from tight geological formations.

Summary

Coupled hydrogeophysics model for effective monitoring of contaminant plumes in subsurface. During FY 2011, we developed and coupled a parallel electric resistivity tomographic (ERT) and complex resistivity inversion code with a reactive transport code (named RAT) that built up INL's MOOSE computing framework. The coupled hydrogeophysics model was successfully applied to monitor the CO_2 plume migration in the subsurface for a synthetic CO_2 injection scenario into a deep saline aquifer. Figure 1 shows the simulation results of this example application. The success of this example application demonstrates the capability and potential of the coupled ERT/RAT hydrogeophysics model for effective and reliable monitoring of migrations of contaminant plumes for environmental management purpose.

Coupled hydrogeophysics model for effective monitoring of hydraulic fracture propagations. During FY 2012, we explored the potential of using electrical geophysical methods to monitor the propagation of hydraulic fractures and the concomitant flow of fracking fluid in the hydraulic fractures, due to the importance of hydraulic fracturing to the development of oil and gas in tight, ultra-low permeability formations (such as shale gas). It is also an extremely challenging problem for both basic science and applied engineering applications. During FY 2012, the PIs have been collaborating with a professor at Colorado School of Mines, Andre Revil, who is the leading expert in electrical geophysics, to couple an electrical self-potential (SP) source inversion model with INL's geomechanics and fracturing model, and investigate the potential of using electrical geophysical methods for effectively monitoring hydraulic fracturing propagations.
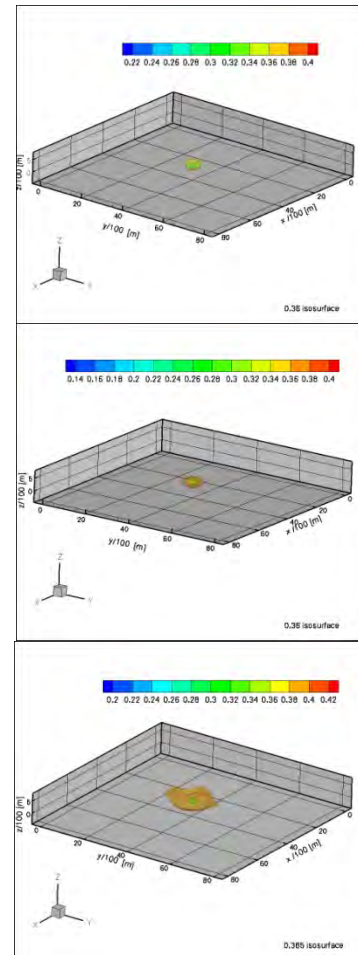
FIGURE 1. Inverted electric conductivity fields from ERT inversion showing the growth and migration of the CO_2 plume.

A proof-of-concept study using the coupled model was performed for a synthetic hydraulic fracturing and SP monitoring test. In this synthetic example, we first ran INL's hydraulic fracturing simulator to generate the propagation process of hydraulic fractures. Each new opening of fractures was then converted into a hypothetic electrical current source. An SP inversion was then carried out to inversely map the new current sources induced by fracturing. The simulation results are extremely encouraging. Figure 2 shows the simulated propagation of hydraulic fracture using INL's fracturing model. Figure 3 shows SP inverse mapping of the locations of newly opened fractures. The close match between the two
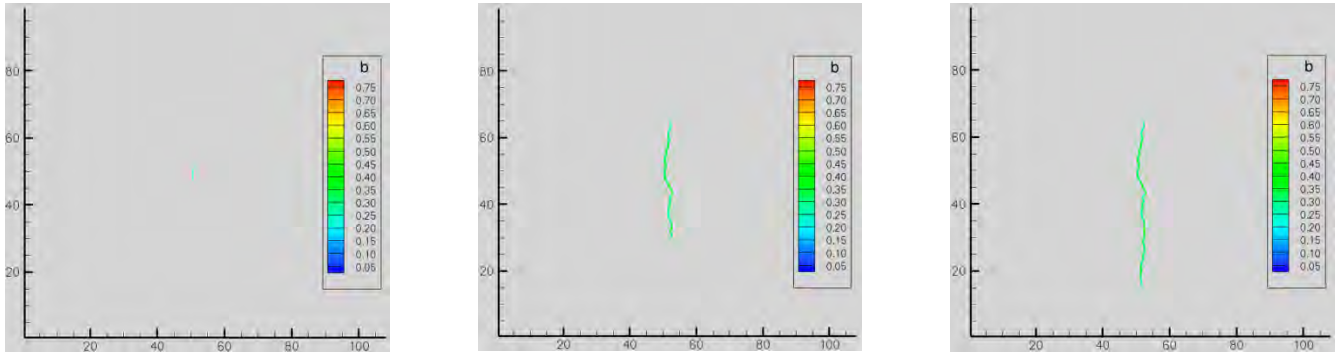
FIGURE 2. Simulated propagation of hydraulic fracture using INL's geomechanics/fracturing model. Colors scale with the fracture aperture.
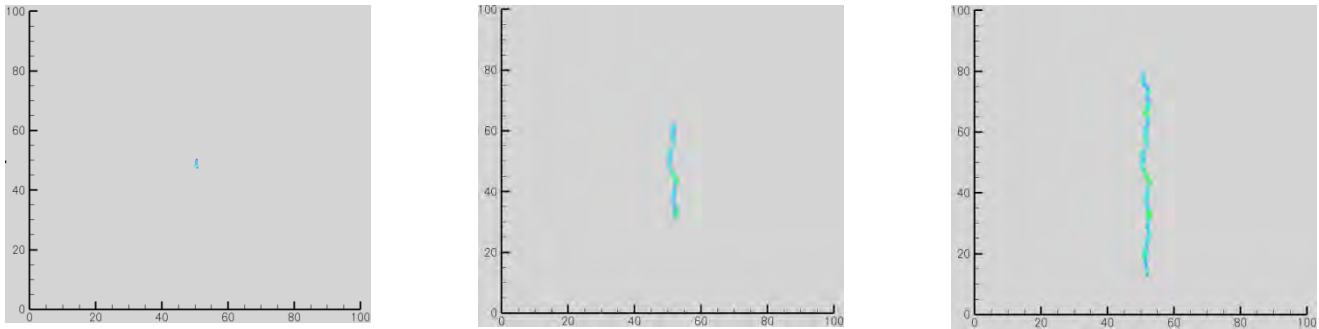
FIGURE 3. Inverse mapping of electrical potential source locations corresponding to the hydraulic fracture propagation process shown in the previous figure.

models indicates that using electrical geophysics might offer an innovative and effective tool for monitoring the hydraulic fracturing process, that typically occurs at great depth (~10,000 ft) in the subsurface, in addition to microseismic imaging which has been the main monitoring technique used by industry.

Benefits to DOE

The successful application of coupling INL's geomechanics/fracturing model with an electrical potential source location inversion model will likely provide more effective and reliable monitoring capability for hydraulic fracturing operations, which is an important topic across the Environmental Protection Agency, DOE, the Department of the Interior, and industry. The novel introduction of ERT inversion to the carbon capture and geological storage community could guide INL's subsurface modeling group into this frontline research

field. This pioneering research of using coupled hydrogeophysics model for monitoring hydraulic fracture propagations will appeal to the hydraulic fracturing community including major oil companies as it offers a better understanding of the fundamental physics that govern hydraulic fracture propagation under a variety of field conditions.

Relevant Publications and Presentations

Lu, C., C. Zhang, and H. Huang, "Feasibility Studies on Field Scale Time-Lapse Electric Resistivity in Monitoring of CO_2 Injection into Deep Saline Reservoir," *International Journal of Greenhouse Gas Control,* 2013. (in preparation)

Huang, H. and A. Revil, "Electrical Potential Source Location Inverse Mapping for Effective Monitoring of Hydraulic Fracturing Process," *Journal of Geophysics*, 2013. (in preparation)

Dynamic Thermo-Mechanical Energy Conversion Simulation

Sam Alessi and Michael Reed

11-064

The intent of this research is to further the understanding of hybrid energy system dynamics through development of multi-physics dynamic modeling tools, including reduced order models for controls integration. We will take advantage and incorporate already existing models as much as possible. Integration of existing models reduces development, verification, and validation costs, and promotes communication and collaboration. These tools can be integrated into concurrently developed dynamic fundamental process and economic evaluation tools to inform energy system-wide dynamic interaction and decision making. This work will create a dynamic prime mover engine model assimilated into a model integration environment, allowing for detailed analysis of unit and sub-unit operations.

The discovery of operating conditions and anomalies that contribute to declining reliability and catastrophic failure of prime mover engines is one application of this hybrid model. Applications of this model will include a variety of prime mover operating conditions and industrial applications to comprehensively investigate the integration of this technology into highly coupled, interdependent unit and sub-unit operations. Portions of this work are fundamental research conducted for the purpose of publishing in the open literature.

The objective of the research was to create a dynamic multi-physics prime mover engine model capable of interfacing with reduced order models and other tools that have been previously developed as part of the Hybrid Energy System (HES) toolbox. These tools are identified in the HES Systems Analysis, Integration, Monitoring and Control Platform including economic evaluation and life-cycle assessments, dynamic and steady-state models for fundamental chemical and thermal processes.

Summary

A 1-D fluid dynamic model was developed and incorporated into the ModelCenter/OASIES integration environment. Next, work proceeded to enhance the OASIES environment for hybrid systems analysis, to gather data and existing models to be integrated and to test integration of existing engine models. It was necessary to research the capability of existing models and select a candidate set that would best meet the goals associated with the desired decisions to be made using the model.

To make the integration environment of greatest utility to a distributed team, novel software was developed to improve the link between ModelCenter and the OASIES web environment. Specifically, software was developed to allow remote web-based users of a hybrid energy systems model to run optimization-based tradeoff studies. The software development involved a strategy for stateless messaging and multi-user processing. The product allows a user to initiate an optimization run where a genetic algorithm chooses the hybrid energy component mix that best meets the optimization goals and constraints. Pareto system alternatives are delivered back to the user as they emerge from the analysis. This allows the user to immediately obtain feedback during a long running optimization.

Tests were conducted of pre-existing engine model code based in Fortran, MatLab, MathCAD, and Aspen. These models all require input data (i.e., parameters, trajectories) and produce an output result set that can include table-like reports and time-based data streams. Each model has its own self-contained data environment. Part of the integration research work is to create a "wrapper" around the existing code. ModelCenter is designed to help the user create the "wrapper" using point-and-click methods (i.e., ModelCenter makes model integration available to researchers who do not write code). Data can then be passed to the legacy model prior to execution and results passed back to ModelCenter when the simulation finishes. Thus, in addition to "wrapper" development, external databases need to be created that encompass the scope of the final hybrid systems simulation to be simulated. Some analysis was conducted to understand the relational database model that would support hybrid systems analysis by analyzing the types of data that are used to run the legacy models at our disposal. The resulting database would provide data that can be used for many uses including statistical model building.

Benefits to DOE

The integrated environment can incorporate models from virtually any federal agency. This project has created an enhanced and very general approach for leveraging existing analysis components of a larger hybrid energy system for the purpose of conducting integrated analysis. A 1-D engine model is currently available and poised to be integrated with other hybrid energy system components associated with energy resources, nuclear power, environmental analysis and social effects. The project is focused on INL's R&D objective, "Advance the Deployment of Secure and Sustainable Energy Systems."

Relevant Publications and Presentations

Grauer, D.K. and M.E. Reed, "Operational Energy for Domestic Installation Energy Islanding: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output," *Energy,* 2012. (submitted)

Grauer, D.K. and M.E. Reed, "Electrical Power Grid Delivery Dynamic Analysis: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output," *American Society of Mechanical Engineers Journal of Engineering for Gas Turbines and Power,* 2012. (submitted)

Grauer, D.K. and M.E. Reed. "Electrical Power Grid Delivery Dynamic Analysis: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output," *Proceedings of the American Society of Mechanical Engineers International Mechanical Engineering Congress and Expo, November 11–17, 2011.* (accepted)

Grauer, D.K. and M.E. Reed. "Dynamic Analysis of Electrical Power Grid Delivery: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output,"

Proceedings of the American Society of Mechanical Engineers Internal Combustion Engine Division Conference, ICEF2011-60170, October 2–5, 2011. (accepted)

Reed, M.E. and D.K. Grauer, "Dynamic Analysis of Prime Mover Combined Heat and Power Delivery to Chemical Processing," *Proceedings of the American Society of Mechanical Engineers Internal Combustion Engine Division Conference,* ICEF2011-60169, October 2-5, 2011. (accepted)

Grauer, D.K. and M.E. Reed, "Electrical Power Grid Delivery Dynamic Analysis: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output," *American Society of Mechanical Engineers International Mechanical Engineering Congress and Expo, IMECE2011-62232, November 11–17, 2011.* (accepted)

Grauer, D.K. and M.E. Reed, "Dynamic Analysis of Electrical Power Grid Delivery: Using Prime Mover Engines to Balance Dynamic Wind Turbine Output," *American Society of Mechanical Engineers Internal Combustion Engine Division Conference, ICEF2011-60170, October 2–5, 2011.* (accepted)

Reed, M.E. and D.K. Grauer, "Dynamic Analysis of Prime Mover Combined Heat and Power Delivery to Chemical Processing," *American Society of Mechanical Engineers Internal Combustion Engine Division Conference, ICEF2011-60169, October 2–5, 2011.* (accepted)

Alessi, S., "Enterprise Model-Based Systems Engineering & Simulation Analysis," *Engineering Design Forum 2012: Emerging Software Innovations, San Diego, CA, May 15–17, 2012.*

Olefin Gas Separations Using Embedded Transition Metal Chelates in Polymeric Membranes

John Klaehn, Aaron Wilson, and Christopher Orme
12-013

Polymeric facilitated transport membranes can be promising for effective separations of olefin (hydrocarbons containing double bonds, e.g., unsaturated hydrocarbons) and paraffin (saturated hydrocarbons) gas mixtures using engineered transition metal complexes of either silver(I) (Ag[I]) or copper(I) (Cu[I]) as transport facilitators. A facilitated transport membrane uses a molecular species that has affinity for a selected species and acts as a shuttle to facilitate transport of the desired species through the polymeric host. Specifically, an olefin (desired species) can be transported preferentially by the metal complex (fixed-site carrier; attached or embedded in the polymer matrix) through the polymer membrane, resulting in more rapid permeation of the selected species over other gaseous components (see Figure 1) that do not have an affinity for the facilitator.

feed gas   **polymer membrane with fixed site facilitators**   **permeate**
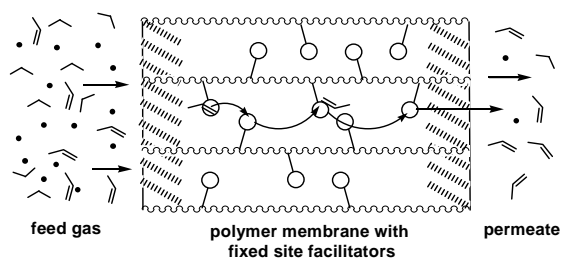
FIGURE 1. Facilitated transport of olefins through a membrane with fixed site facilitators (propylene, propane, and other gases).

Facilitated transport will have a great economic impact for olefin separations. Olefins are needed as feedstocks to the production of plastics and fine chemicals. Olefin production is a multibillion dollar industry that uses several different refinery processes to generate olefinic products. The typical route to olefin production is the fossil fuel catalytic cracking process. However, this process produces both olefins and paraffins at the same time. Since olefins and paraffins have similar molecular sizes and boiling points, separation of these two products is difficult. The "state of the art" for the industrial separation of olefins and paraffins uses energy intensive cryogenic distillation. In addition, the energy that is needed for this cryogenic process can use the composite gas stream (olefin/paraffin) as a source to power the compressors,

resulting in parasitic loss of product. It is estimated that 120 trillion Btu/yr are consumed for olefin/paraffin separation in the U.S. As a result, the energy cost associated with making polymer grade olefins combined with the raw material cost makes these chemicals relatively expensive. Our approach creates an energy efficient membrane-based olefin separation process that operates at near ambient or slightly elevated temperatures—reducing energy costs for this separation.

Olefin separation has been examined for over four decades, and the best performance has been achieved by Cu(I) and Ag(I) ions as transport facilitators. Cu(I) and Ag(I) metal ions preferentially complex with and facilitate transport of the olefin as a gas/vapor through a polymer membrane host, giving excellent permeability and high selectivities favoring the desired olefins. The shortcoming of previous work is the use of Cu(I) and Ag(I) metal ions in a loosely bound or "naked" state in the polymer matrix. Facilitation is lost over time due to poorly defined coordination spheres, metal ion leaching, deactivation through oxidation/reduction, and sintering into inactive clusters. To address these deficiencies, incorporation of metal ions into polymer membranes is a research problem at the boundaries of membrane science and coordination chemistry.

Summary

Initially, a metal chelate, which provides metal stability and olefin transport characteristics, had to be designed and synthesized. We used a new route to synthesize the proposed multidentate heteromacrocycle as a free ligand, and it enabled new coordination chemistries for late-transition metals with an excellent complex geometry and an effective support. In addition, the synthesized compound can be functionalized, which can assist in solvent solubility and enables an attachment point to other molecules. The synthesized compound is a ligand featuring multiple soft heteroatom (e.g., phosphorus) donors ideal for coordination with late-transition metal centers in all oxidation states. In addition, the synthesized compound provides Ag(I) open coordination sites leaving them accessible to facilitate transport of olefins.

Our team synthesized the new ligand, and isolated the subsequent Ag(I) complex in good yields. The isolated Ag(I) complex was chemically characterized using multi-nuclear Nuclear Magnetic Resonance (NMR) spectrometry. The Ag(I) complex showed excellent stability towards aggressive organic solvents (e.g., dimethylsulfoxide and acetic acid), light, temperature, and atmospheric exposure. It should be noted that most silver salts are not able to withstand these conditions, and they will discolor in solution and potentially precipitate. Preliminary ^{1}H NMR analysis showed that Ag(I) will interact with the double bond on alkenes, suggesting potential activity of this new complex as a facilitator.

Once characterized, the facilitator was embedded in a polymer membrane. We initially chose poly(dimethylsiloxane) (PDMS) because of its well understood gas transport behaviors and its ready availability. A mutual solubility approach was taken where it was desired to find a solvent that would dissolve both the Ag(I) complex and the polymer. The Ag(I) complex was found to be soluble in polar organic solvents (like, acetone or acetonitrile). Unfortunately, PDMS was not soluble in polar organic solvents, thus development of casting solutions was not possible. Other polymers, like polyethylene glycol (PEG) and polyphosphazenes were better at making casting solutions with the facilitator. The Ag(I) complex can be incorporated into different polymer solutions without phase problems, up to 1:1 by weight with the facilitator and polymer. Another alternative to PDMS casting solution method was the use of flat sheet PDMS membranes as support for the facilitator/polymer mixtures. Interestingly, none of the metal-embedded polymer films changed color over time when exposed to the atmosphere, suggesting that the metal complex was chemically stable within the polymer.

Gas permeability analysis of the membranes was performed using a catalytic cracking gas simulant containing hydrogen, methane, ethane, and ethylene, where permeabilities of each component were used to calculate membrane selectivity. Our team found that the best results were obtained using a mixture of the facilitator and PEG that was cast on a PDMS membrane/support. The preliminary gas permeability data showed a preference for olefins when the facilitator was added to the system. Further studies are needed to determine the parameters,

such as facilitator loading and membrane thickness that will provide optimized olefin/paraffin separation.

A successful outcome of the project was the positioning INL for partnerships and target future funding opportunities. This year, INL obtained funding from Compact Membrane Systems, Inc. through a DOE-Small Business Technology Transfer (STTR)-Small Business Innovation Research (SBIR) grant to develop a related technology that leveraged the outcomes of this work. This shows that the INL approach to these types of separations has market appeal and the potential to solve this chemical separation problem.

During this project, a successful set of "proof-of-concept" experiments has been completed, including: a viable synthetic pathway for the facilitator, blending the facilitators into polymers, and obtaining positive data from preliminary gas permeability analysis. We anticipate that the data obtained from this project will offer intellectual property disclosure opportunities. Once the intellectual property position is secure, several publications and presentations will be made from this work.

Tangible Accomplishments (FY 2012)

- Synthesized and isolated a multidentate chelate to Ag(I). This is the first known instance of this chelate, and its stability is excellent towards temperature, light and solvents compared to other Ag(I) salts.

- The synthesized Ag(I) chelate has been successfully mixed with polymer solutions to form thin film membranes. These facilitator embedded membranes have been analyzed for their preliminary gas separation performance, and they assist olefins over paraffins.

- A patent application has been submitted to the U.S. Patent and Trademark Office and other invention disclosure records are possible.

- Future opportunities - collaborations and/or funding.

  – Continuing work with Compact Membrane Systems, Inc.

  – Collaborating with Dow, Air Products, Aire Liquide, and General Electric, who will be interested in improving their present technologies and possibly pursuing funding opportunities.

137

- – Funding opportunities from DOE-Office of Fossil Energy.

- – Defense Advanced Research Projects Agency, Office of Naval Research for O_2 separations and CO_2 sequestration, and Army Research Office for fuel sources.

Benefits to DOE

DOE, through the Offices of Fossil Energy and Energy Efficiency and Renewable Energy, will benefit from this new capability in improved olefin separations, and this technology also fits into INL's Advanced Manufacturing Platform where specific gas separations are needed (such as isobutylene and carbon monoxide separations). INL is recognized for its contributions to gas separation research using polymer membranes, which provides a significant benefit for DOE, INL, the region, and the nation, by enabling new economically advantageous industrial focused chemical separations. Industries where this technology can benefit include the petrochemical and manufacturing sectors. Overall, industry can benefit by the adoption of new energy efficient separation processes, which also benefits consumers by reducing the costs of products in the marketplace.

Relevant Publications and Presentations

None.

A Novel Bioreactor to Study the Human Microbiome

Vicki Thompson, William Apel, Joni Barnes, Dayna Daubaras, and David Reed
12-046

Growing evidence in literature shows that the complex array of microorganisms indigenous to the human body (human microbiome) has a profound influence on human health and disease. Cardiovascular disease, obesity, metabolic syndrome, diabetes, peptic ulcers, colitis, and late onset autism all appear to have links to the presence/absence and/or changes in abundance of these microorganisms. Due to the location of many of these organisms in the human small and large intestine, studying them in a systematic way is difficult. Animal models are commonly used, but are complex, difficult to control, and often not representative of human physiology. Another way to reliably conduct these types of studies is needed. This project builds upon the established expertise at INL in microbiology and biochemical engineering to meet this need by designing a bioreactor system that mimics the major processes occurring in the human large intestine. Once developed, we tested this system by challenging the reactor microorganisms with an antibiotic and determining their response.

Summary

There are a number of processes that occur in the large intestine including water absorption, ion absorption and secretion, biofilm formation with associated nutrient gradients, pH gradients, mixing, and residence time. The reactor consisted of two vessels approximately 1 L in volume containing 300 mL of nutrient medium and 90 mL of gellan/xanthan gum beads. These two reactors were designed to simulate the medial and distal regions of the large intestine with appropriate flow, mixing, pH, and residence time distributions. The pH of Reactor 1 was controlled at 6.2 and the pH of Reactor 2 at 6.8. The overall flow rate was adjusted to provide a residence time of 12.5 hours for each reactor, which is comparable to physiological times. Each reactor was kept well mixed with a recycle loop set at a flow rate of 20 times the residence time flow rate. When connected, the two reactors simulated a plug flow with mixing model that approximates the physiological system. The nutrient medium fed into Reactor 1 was developed based upon literature formulations and was designed to simulate the material exiting the small intestine of an infant. The gel beads were present to simulate solid particles present in the large intestine and provide surface area for microorganisms to form biofilms which is an important process physiologically. The nutrient medium was kept anaerobic

by sparging with nitrogen and carbon dioxide and the reactor system was submerged into a water bath to maintain the physiological temperature of 37°C. A hollow fiber cartridge with a 3000 Da molecular weight cutoff membrane was positioned between the two reactors. The liquid effluent from Reactor 1 was pumped through the shell side of the cartridge and a 2% solution of 10,000 Da molecular weight polyethylene glycol (PEG) containing 30 mM sodium, 80 mM potassium, and 45 mM bicarbonate was pumped through the tube side. Since the PEG was unable to pass through the membrane, the resulting osmotic gradient in the cartridge caused water to be absorbed from the Reactor 1 effluent. The ion concentrations in the PEG solution represented those exiting the distal portion of the large intestine and, compared to the concentrations in the effluent coming from Reactor 1, resulted in a net absorption of sodium and bicarbonate ions and a net secretion of potassium ions into the fluid entering Reactor 2.

Inoculum for the reactor was obtained from three infants (two boys and one girl) ranging in age from 3-9 months. Two of the infants were breast-fed and the other formula-fed. The 9-month-old infant was just starting to receive solid food. We hoped that pooling these samples would provide a representative sample for an infant microbiome. The fecal material was extracted, pooled, and homogenized. This material was inoculated into Reactor 1 and allowed to incubate for 24 hours without flow to establish gel bead biofilms. Flow was then started and Reactor 2 was inoculated from the effluent of Reactor 1. Liquid samples were withdrawn from both reactors on a daily basis and analyzed for fatty acids as a marker for metabolic activity in the system. The fatty acid concentrations in both reactors stabilized after approximately 15 days and this point was designated as the initial steady state. At this time, gel beads from both reactors were sampled in duplicate to assess the steady state microbial community. Reactor 1 was then challenged with Ciprofloxacin and was dosed twice daily for seven days at a dosage comparable to what an infant would receive. After the antibiotic challenge, bead samples were again taken from each reactor in duplicate. The samples were extracted to obtain genomic DNA which was sent to Second Genome, Inc. for PhyloChip microarray analysis. This technology was originally developed at Lawrence Berkeley National Laboratory and

has been expanded to include many microbial taxa representative of the human gastrointestinal system.

The Phylochip analysis examined the microbial community of the samples from each reactor at steady state and post Cipro treatment as well as the original infant fecal material inoculum. The communities were examined in two ways: presence/absence of microbial taxa and abundance changes of microbial taxa between samples. In general, it was found that the infant inoculum, the initial steady state and the post Cipro samples all had different microbial community structures both in terms of presence/absence and abundance. This was the expected result between the steady state and post Cipro samples. While it was originally expected that the infant inoculum and the steady state samples would be similar, in retrospect the result obtained makes sense when considering that the infant fecal material represents the community present after material transits the entire large intestine while the steady state reactors were meant to simulate only the initial portion of the large intestine. Another finding was that Reactors 1 and 2 had different microbial communities,

which indicates that the reactor system succeeded in demonstrating the expected physiological response. Analysis of the results from this dataset is still ongoing.

Benefits to DOE

This project directly supported DOE's science mission which seeks to "strengthen U.S. scientific discovery, economic competitiveness, and improving quality of life through innovations in science and technology." In particular, this project has developed a unique tool that can be used to study a variety of questions about the human microbiome and its effects upon many important health issues. This project also supports other federal agencies including the Department of Defense, the National institutes of Health, and the National Aeronautics and Space Administration. Each of these agencies have expressed interest in the human microbiome in terms of soldier health, overall human health and astronaut health on long term missions, respectively.

Relevant Publications and Presentations

None.

Thermo- and Acid-Stable Enzymes for Improved Animal Feed Nutrient Digestion

William Apel, Brady Lee, and Vicki Thompson
12-051

The application of enzyme mixtures to improve nutrient recovery from plant-based feeds by mono- and poly-gastric animals is an area of industrial biotechnology where thermo- and pH-stable enzymes will lead to improved nutrient delivery to animals. The primary goal of improved feed utilization is to increase animal production through optimized delivery of nutrients with concurrent minimization of animal wastes. Commercial application of enzymes has primarily focused on grain-based animal diets. According to the literature, development of enzyme mixtures for enhanced utilization of non-grain plant material is needed. In addition, pelletization of animal feed is a method of improving feed quality and uniformity, but application of enzymes to these mixtures requires enzyme stability at temperatures in excess of 80°C, followed by enzyme activity at temperatures, pHs, and in the presence of digestive enzymes found in animal digestive tracts. The ultimate goal of this project is to develop enzyme cocktails that are stable after exposure to: (1) high temperatures (>70°C) associated with pellitization processes; and (2) low pHs associated with the upper digestive tract of non-ruminant animals. In addition, activity over pH ranges present in animal digestive tracts will also be important in developing optimum enzyme activity and production of nutrients that will improve animal production, as well as giving the added benefit of decreased pollution from animals. Our approach is innovative since it takes advantage of properties possessed by many extremophilic enzymes. Our previous work with these enzymes has shown that a number possess broad activity profiles across a range of conditions while exhibiting stability to high temperatures and/or low pHs. As such, the development of these enzymes for use in animal feeds provides a unique approach for optimizing enzyme stability for feed processing as well as optimized nutrient delivery in the animal. This will lead to increased animal production while decreasing environmentally deleterious components such as ammonia and phosphorous in the animal waste.

Summary

We originally proposed surveying hot spring metagenomes for potential enzymes that could be applied for the processing of animal feed. These enzymes include glycosyl hydrolases, such as, xylanases, cellulases, pectinases; and amylases, lipases, proteases, and phytases. During FY 2012, the decision was made to no longer support this LDRD after FY 2012. For this reason, we shifted our approach to screening hot spring isolates in our collection for enzymes with the activities we sought. We made this change because a metagenome approach (our original proposal) would require the production of recombinant enzyme, which would not have been feasible for a one-year project. These isolates were initially selected for growth on hemicellulose, and research from other laboratories indicated that some of the species may be able to produce other enzymes of interest to the project.

Isolation Selection. Thirty-two thermophilic bacterial isolates that were enriched from ground corn stover, corn cob, or lodgepole pine that had been shallowly buried in soil in a hot spring, were enriched on birchwood xylan. Our goal was to focus on isolates that produced extracellular enzymes. In addition to xylanolytic activity, a number of these isolates demonstrated the capacity to produce other hydrolytic enzymes. Initial screening narrowed the number down to six: two *Geobacillus subterraneus* species, two *Geobacillus thermoleovorans* species, and two *Anoxoybacillus kamchatkensis* species.

Isolate Screening. Screening of the bacterial isolates for activities that are applicable for the enzymatic processing of non-grain plant material for plant feed was accomplished using media containing substrates and indicators that demonstrated the extracellular enzyme activity of interest. Xylan was used for xylanase activity; carboxymethylcellulose (known as CMC) was used for cellulase activity; apple pectin was used for pectinase activity; wheat starch was used for amylase activity; olive oil with rhodamine B was used for lipase activity; casein or skim milk was used for protease; and phytic acid was used for phytase activity.

Results from this screening indicate that all of the isolates showed extracellular pectinase activity, both *G. subterraneus* species demonstrate extracellular xylanase and cellulase activity. Only one other isolate showed slight xylanase activity; none of the other isolates showed cellulase activity. Five of the six isolates demonstrated amylase activity. Only one of the isolates, *G. thermoleovorans*, demonstrated lipase activity (see Figure 1). Interestingly, this was the only isolate that showed protease activity during screening. To date, none of the isolates demonstrated the ability to hydrolyze phytic acid.
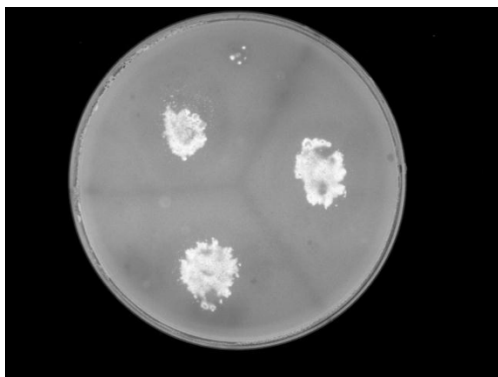
FIGURE 1. Photo of *Geobacillus thermoleovorans* colonies that produce lipase.

Benefits to DOE

A core theme of DOE is to "strengthen U.S. scientific discovery, economic competitiveness, and improving quality of life through innovations in science and technology." This work supports this DOE theme area since it directly links to supporting economic competitiveness in the area of stable enzymes through our immediate links to industrial entities such as Novus International.

This LDRD project will expand our expertise in extremophilic enzymes related to the processing of biomass. In addition to the applicability to plant biomass for animal feed the enzymes developed may have applications in other industrial sectors. Enzymes developed could be added to stored plant biomass prior to pretreatment and conversion to ethanol, potentially decreasing pretreatment time and severity of the process, which will also bring down the cost of bioethanol production.

Relevant Publications and Presentations

Lee, B.D., V.S. Thompson, and W.A. Apel, "Production of Extracellular Lignocellulose Hydrolyzing Enzymes by a Thermoalkaliphilic *Geobacillus Subterraneus* Species Isolated from an Oregon Hot Spring," *Applied Microbiology and Biotechnology,* 2013. (in preparation)

Lee, B.D., V.S. Thompson, and W.A. Apel, "Characterization of Thermoalkalophilic Lipase and Protease Enzymes from *Geobacillus Thermoleovorans* Isolated from Hot Springs in the Alvord Desert in Oregon," *Applied Biochemistry and Biotechnology*, 2013. (in preparation)

Development of Unique Nanomaterials for Selective Replacement of Strategic and Critical Materials

Robert Fox and Joshua Pak[1]

12-093

According to literature, the U.S. lighting market is estimated to be valued at approximately $27B annually, with a worldwide market value of $110B annually. DOE estimates that across all sectors (residential, commercial, industrial, and outdoor) light generation in the U.S. is responsible for more than 25% of the entire annual U.S. electrical energy consumption. The DOE roadmap for solid-state lighting anticipates solid-state lighting (SSL) to gain significant commercial market share over the next decade, especially with the imminent phase-out of inefficient incandescent bulbs that do not meet the Energy Independence and Security Act of 2007 efficiency standards. Switching from conventional lighting to SSL is important not only for reducing consumption of electricity and fossil fuels, but also for decreasing growing dependence on fossil fuel-based electricity and consequent greenhouse gas emissions.

Current commercial SSL technologies rely heavily on rare earth phosphors. Literature states that the past decade of research in this area has been dominated by the development of rare earth-doped phosphors. Light-emitting diodes (LEDs) using rare earth-doped phosphors currently dominate the commercial SSL market. Recent export constraints placed on rare earth elements (REEs) by China, coupled with rising cost (doubling and tripling), limited availability, and increased worldwide competition for rare earths, has placed new emphasis and urgency on research into energy-efficient light-emitting materials which are free of REEs.

This project focuses on synthesis of ternary, quaternary, and doped metal chalcogenide quantum dots arranged in hybrid and core-shell architecture that are specifically designed to replace rare earth phosphors in solid-state lighting applications. Highly luminescent semiconductor nanomaterials, having high quantum-yield and stable thermal performance, are ideal for high power and/or high energy-density applications such as those found in LEDs, laser diodes (LDs), and energy-efficient solid-state lighting. The latest research in SSL phosphor technology has shown that metal chalcogenides and doped metal chalcogenides are best suited as rare earth phosphor replacements in all three current white light-emitting diode commercial designs. For this LDRD project, new nanomaterials will be synthesized based on known and successful metal-organic precursor chemistry using established precursor decomposition techniques which yield nano-phase metal composites and alloys having materials properties similar to or superior to strategic and critical elements currently in use. Specifically, this work will focus on synthesis of ternary, quaternary, and doped metal chalcogenide nanomaterials (quantum dots) arranged in nano-alloy and core-shell architecture which will replace rare earth phosphors found in energy-efficient phosphor-converted lighting, especially white light-emitting diodes. Unique semiconductor nanomaterials will be synthesized and their electro- and photoluminescence properties examined.

Summary

This activity is divided into three tasks. Each task has performance criteria by which success can be measured and progress can be noted. Tasks are explained in further detail below:

- Task 1: Synthesis and characterization of the targeted metal-organic precursors

- Task 2: Solvothermal decomposition of precursors into targeted nanomaterials

- Task 3: Characterization of nanomaterials.

In FY 2012 we selected two nanomaterial compositions to synthesize and characterize. The first material being a core-shell quantum dot comprised of a $CuInS_2$ chalcogenide core, covered with a ZnS shell. The second material being an alloy comprised of $(ZnSe)_x (CuInSe_2)_{1-x}$. Ultimately, we desire to demonstrate synthesis of such nanomaterials using a multi-step solvothermal decomposition process that employs single-source organometallic precursors (SSPs) as the starting materials. Whereas our FY 2012 effort synthesized some alloys and core-shells using conventional routes, considerable effort was put into developing new SSPs. Thus, Task 1 Synthesis and Characterization of SSPs, involved efforts on two fronts: the first effort being synthesis of SSPs for microwave/supercritical fluid solvothermal decomposition to form core $CuInS_2$ materials, which were then covered with ZnS or ZnSe using a conventional chemical approach; and, the second effort being development of new organo-zinc derivatives that would serve as SSPs for microwave/supercritical fluid

solvothermal decomposition to form a shell over the core $CuInS_2$ material.

In FY 2012, synthesized, nanomaterials were characterized (Task 3, Materials Characterization) to both confirm their materials properties and their chemical composition.

Benefits to DOE

The development of high-efficiency luminescent materials that are not based on rare earth phosphors is a cross-cutting issue for multiple DOE branches and programs including the Next Generation Lighting Initiative, Basic Energy Sciences Program, Solid State Lighting Program, Energy Efficiency and Renewable Energy Building Technologies Program, and Advanced Research Projects Agency-Energy, as well as an upcoming DOE focus area involving replacement, recycle, reduction and reuse of energy critical elements such as rare earths. Successful synthesis of replacement phosphors for solid-state lighting will favorably impact DOE programs and allow for Roadmap milestones and performance criteria to be met.

This project will benefit DOE environmental quality goals and objectives by developing and advancing "green" nanosynthesis technology that is specifically designed to reduce, reuse, recycle, and recover chemicals used in commercial-scale materials manufacturing processes. Successful generation of targeted luminescent materials and successful adaptation of our solvothermal synthesis process to make luminescent materials will provide U.S. industry an advantage by reducing overall environmental liabilities through reduction of hazardous chemical used in materials synthesis processes. If successful, this work will result in a more rapid advancement of energy-efficient solid-state lighting into the commercial market by replacing rare earth phosphors with commercially-attractive materials. A more rapid entry of solid-state lighting into the U.S. lighting market will reduce U.S. electricity consumption and dependence on non-domestic energy sources. Thus, successful outcome of this LDRD will advance the deployment of secure and sustainable energy systems.

Relevant Publications and Presentations

Publications are planned for FY 2013 after capture of key materials properties data.

Unmanned Aerial Vehicle-Based Remote Sensing and Data Fusion for Energy and Environmental Applications

Matthew Anderson, Ryan Hruska, Nancy Glenn,[1] and Jessica Mitchell[1]
12-094

The development of advanced remote sensing capabilities using unmanned aerial vehicles (UAV) contributes to a wide range of research areas supported by DOE and INL. This research project has three objectives that result in advancing the state-of-the-art in environmental remote sensing, data collection, and analysis using UAVs: (1) develop a data fusion research application that integrates terrestrial laser scanning with UAV-based data, (2) develop airborne LiDAR data collection capabilities for lightweight UAVs, and (3) demonstrate unique multi-scale and multi-sensor data acquisition and analysis. A biomass demonstration capitalized on recently acquired INL remote sensing datasets for 3-D visualization and the development of data fusion techniques. Airborne biomass estimates support fuel load mapping and can be extended to agricultural productivity metrics. To accomplish the second objective, a commercial- off-the-shelf LiDAR sensor will be integrated on the INL's UAV airframes during year two efforts for precise geo-location of the resultant data. To accomplish the third objective, spectral and LiDAR sensor platforms (ground and airborne) will be optimized in terms of data quality and operational parameters to acquire and integrate a collection of spatial data. By performing this research, INL will have the capability to provide a suite of platforms to collect data needed by scientists in order to understand and monitor complex/changing environmental issues related to energy management. Examples include thermal anomaly detection for geothermal exploration and LiDAR/hyperspectral fusion for biomass estimation.

Summary

Year one efforts included the addition of two post-doctoral researchers working in the area of data fusion with data sets from multiple sensors and ground- and aerial-based remote sensing platforms. The data fusion framework was designed to include lower level tasks such as processing raw sensor data and correlating data across sensors as well as higher level tasks such as analyzing composite data products, developing predictions from the composite products, and iteratively assessing and refining prediction accuracy. Initial data analysis was conducted on combined data sets from the Bureau of Land Management and INL UAV team of the Orchard Training Area (OTA) as seen in Figure 1. The OTA is located near Boise, Idaho on the Birds of Prey National Conservation Area. A direct comparison of shrub cover in the unsupervised classification to shrub cover in the existing OTA shrub map indicates close correspondence.
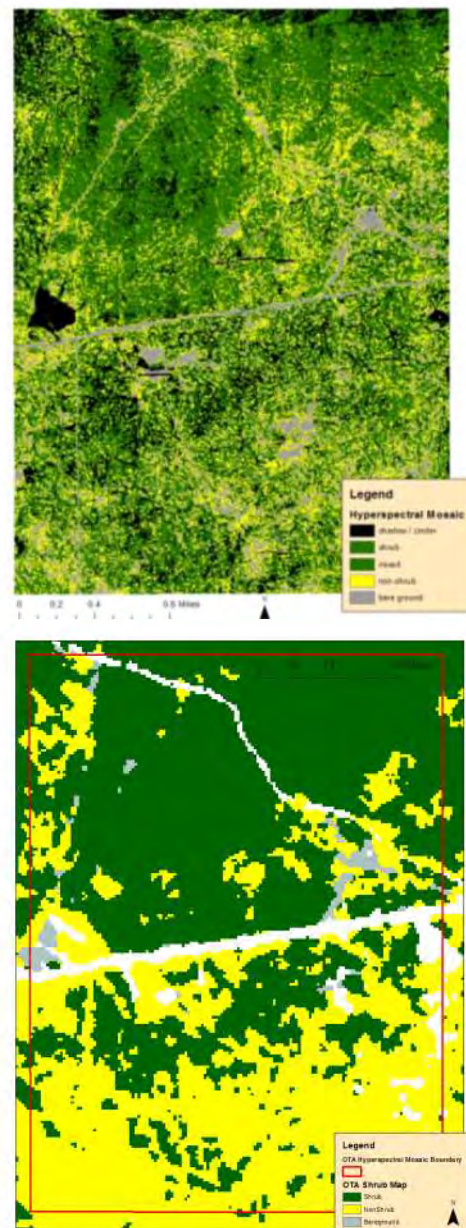
FIGURE 1. Comparison of: (top) unsupervised classification results for the OTA hyperspectral (PIKA II) mosaic (2010) to (bottom) an OTA shrub map derived from 2000.

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[1] Idaho State University

145

A second data fusion effort was conducted to perform vegetation cover and volume estimates in semi-arid rangelands using LiDAR and hyperspectral data from data sets acquired at INL near the UAV runway. Multiple regressions were performed to analyze the benefit of combining the derived LiDAR vegetation cover and hyperspectral imagery. The resulting equation was used with an object-based image analysis of the area. Objects were created from a LiDAR-derived vegetation cover using the red edge position index (the ratio of reflectance at 750 nm to that near 700 nm) as well as a LiDAR derived vegetation cover raster. Preliminary results show a potential relationship between field measured sagebrush vegetation cover and LiDAR and field measured sagebrush vegetation cover and hyperspectral indices (see Figure 2). This relationship also appears to be strengthened when the two are combined. However, work is still needed for applying relationships to object-based image analysis.

Vegetation Cover (%)

Color	Value
	Low
	0.000001 - 5.000000
	5.000001 - 10.000000
	10.000001 - 20.000000
	20.000001 - 30.000000
	30.000001 - 40.000000
	40.000001 - 50.000000

0   0.05   0.1 km

N
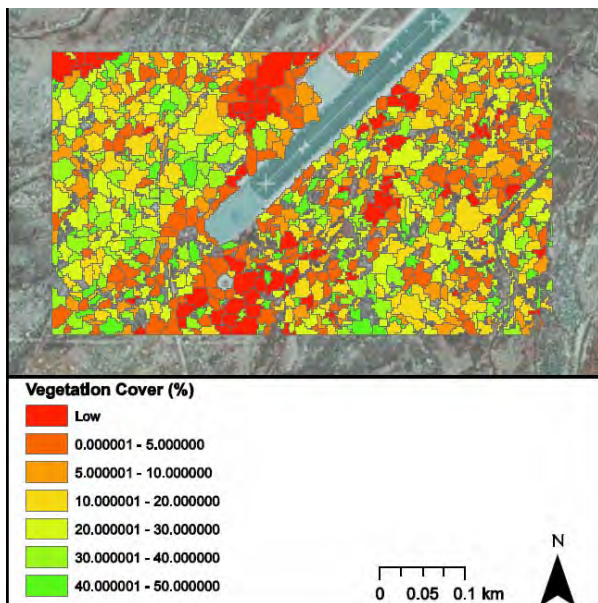
FIGURE 2. Vegetation coverage map created using multiple regression equation and object based image analysis.

Additional efforts were underway to evaluate commercially-available LiDAR sensors suitable for UAV-based data acquisition. As part of this effort, a fluorescence study was being conducted to select optimal excitation and emission wavelengths suited for detecting fluorescent signals directly related to the content of chlorophyll and other pigments in plants suitable for identification of plant species and possibly plant health.

Benefits to DOE

The UAV-based remote sensing capabilities derived through this research contributes directly to DOE's mission of advancing the national, economic, and energy security of the U.S. by providing the base capabilities required for the collection and assimilation of remote sensing data. This enhances DOE's capabilities to monitor water availability, disaster response and hazardous and radioactive waste sites in order to protect human health and the environment, track management activities, and improve the ability to meet specific DOE orders, such as DOE O 450.1, Environmental Protection Program – Directives, relating to implementing sound environmental stewardship practices. This will ensure the productive and optimal use of our Nation's energy and environmental resources.

Relevant Publications and Presentations

Hruska, R., J. Mitchell, M. Anderson, and N. Glenn, "Radiometric and Geometric Analysis of Hyperspectral Imagery Acquired from a Medium Altitude, Long Endurance Unmanned Aerial Vehicle," *MDPI Remote Sensing Journal* (special issue on UAVs based Remote Sensing, http://www.mdpi.com/journal/remotesensing/special_issues/uav), August 17, 2012.

Mitchell, J., N. Glenn, M. Anderson, R. Hruska, A. Halford, C. Baun, and N. Nydegger, "Unmanned Aerial Vehicle (UAV) Hyperspectral Remote Sensing For Dryland Vegetation Monitoring," *IEEE WHISPERS 2012–4th Workshop on Hyperspectral Image and Signal Processing Evolution in Remote Sensing, Shanghai, China, June 5, 2012*.

Isolation and Purification of Critical Metals Using Ionic Liquid-Based Solvent Extraction

Aaron Wilson, John Klaehn, Eric Dufek, and Mark Ogden
12-096

Room temperature ionic liquids (RTIL) are needed for the extraction and separation of targeted strategic and critical materials (S&C) that feature a non-polar anionic extractant and a non-polar non-coordinating cation. The synthesized materials developed in this project were generated from existing extractants, which avoids costly empirical experiments that produce extractants of unknown quality and behavior. Dual extractant nonpolar RTIL are recyclable, may allow reduced processing volumes, avoid problems associated with volatile organic solvents, and allow for novel separation and processing methods targeting S&C materials.

Specifically, this work involves the synthesis and characterization of innovative material RTIL and salting agents, extraction studies, and exploration of electrowinning with such materials. We are evaluating and reassessing the industrial practicality of working with these materials and the associated methods for the separation of S&C materials.

Summary

We have produced three dual extractant nonpolar RTIL on a 20 g scale including: hexadecyltributylphosphate (2,4,4-trimethylpentyl)-dithiophosphinium (HDTBP:Cyanex 301), butyldecyltrihexylphosphate (2,4,4-trimethylpentyl)-dithiophosphinium (Cyphos:Cyanex 301) butyldecyltrihexylphosphate 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dionate (Cyphos:TTA). In addition, sodium 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dionate (NaTTA) as a salting agent. These materials have been comprehensively characterized by nuclear magnetic resonance and electrochemically though cyclic voltammetry and other applied potential experiments.

In parallel, we explored means to enhance electrowinning in RTIL, which suffers from mass transfer issues. The methods that we developed are contained in the invention disclosure record (IDR) BA-699, "Method to enhance electrodeposition rates in ionic liquids." It was found that the electrochemical window of the extractant RTIL was not sufficient for electrowinning most S&C. While our methods are promising for other applications and with RTIL featuring wider electrochemical windows these experiments were not pursued in this LDRD.

The extraction capacity of the dual extractant, nonpolar RTIL have been studied using several matrices of rare earths, which include Ce(IV), Sm(III), Y(III), Yb(III), Eu(III), and Tb(III). The RTIL extractant composition was varied to comprise of neat RTIL, hexane/RTIL mixtures, and various degrees of Na(X) and phosphonium(Cl). The separation factors of targeted S&C ions were calculated based on concentration data from inductively coupled plasma mass spectrometry results. The extraction performance has been very promising for the Cyphos:TTA system. These preliminary studies have also studied pH dependence for the Cyphos:TTA system and the data showed to be competitive with existing extractant systems. Figure 1 shows that the determination the maximum concentration of S&C ions is ongoing.
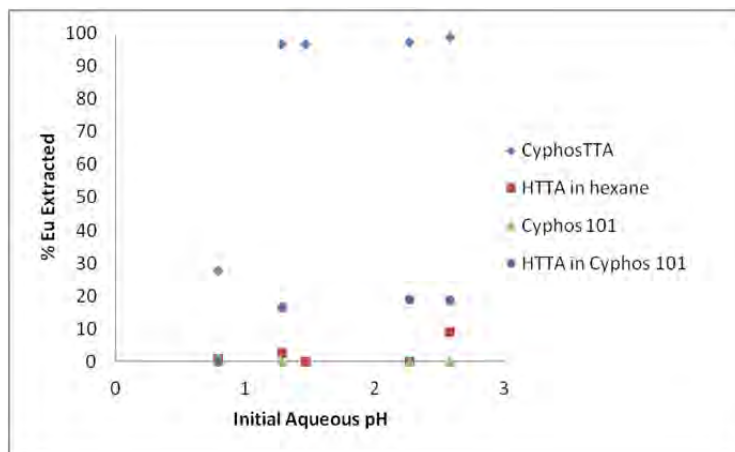
FIGURE 1. Fraction of Eu extracted by a variety of extractant compositions over a range of pH.

Benefits to DOE

The importance of S&C is significant to U.S.'s economic and defense future. Research into S&C furthers DOE mission objectives to, "Discover, develop, and deploy innovations that advance the critical infrastructure systems," and "Advance the deployment of secure and sustainable energy systems."

Relevant Publications and Presentations

None.

Designing Algal Biofuel Consortia for Increased Function and Reduced Nutrient Costs

James Henriksen, William Bauer, Joni Barnes, and Deborah Newby
12-099

Algae are an excellent platform for multiple applications in biofuel and energy generation, as well as CO_2 sequestration and organic synthesis. To be economical at a large scale, lipid-producing eukaryotic algae must be cultured in large open pools, and nutrient addition costs must be minimized. However, in state-of-the-art pools, unutilized wavelengths of light and added nutrients are available for other organisms that compete with the desired algae, resulting in decreased productivity and pond population crashes.

The principle goal of this project is to design and develop mixed prokaryotic consortia as a means to improve the stability, productivity, and economics of algal cultivation. Cyanobacteria and other photosynthetic organisms can utilize wasted light energy and also fix nitrogen, and/or provide growth factors thereby increasing biomass yield. In order to construct effective consortia for enhanced biofuels production, these types of organisms must be identified, characterized, and monitored (Figure 1). To achieve this, the project is establishing an INL archive of phototrophic microbes including algae, cyanobacteria, and algal pond contaminants, and developing a spectral database of pure and mixed cultures using hyperspectral fluorometry. We are using the database to evaluate and guide selection of beneficial consortia members and develop a low cost real-time method for monitoring algal co-cultures. Finally, engineered consortia testing and scale up studies are being conducted.

Summary

To establish a culture collection for spectral analyses and consortia development, a diverse group of phototrophs was acquired, cultured, and preserved. Currently, the project maintains a suite of 24 phototrophic microorganisms including commercially significant eukaryotic algae, a variety of cyanobacteria and several aerobic anoxygenic phototrophic bacteria (AAnP). These microbial groups represent the major types and combinations of photopigments found in light absorbing microorganisms.

Although algal and cyanobacterial members of the collection were obtained from the INL biofuels program and bioresource centers (Marine Biology Laboratory, Woods Hole Massachusetts, and Carolina Biological Supply Co.), the AAnPs were isolated by the project from INL algal raceway cultures. In this work, 16S ribonucleic acid sequencing of isolates with characteristic AAnP pigmentation identified two species closely related to the AAnP *Porphorybacter.* This result corroborates previous metagenomic studies at INL and provides evidence that this group is a common and perhaps important member of algal consortia.

As cultures became available, the spectral characteristics of mixed and pure cyanobacteria and algal cultures were determined using laboratory spectrophotometers and fluorometers. Fluorometry excitation and emission wavelength scans were performed such that light-harvesting pigments from each organism could be resolved, creating a unique fingerprint for specific members of each group. Differences in spectral features were determined using chemometric multi-way data analysis. Results provided evidence that the methodology, which reveals diagnostic wavelengths, can be used to differentiate, identify, and quantitate algal and non-algal members present in mix cultures and provide a platform for the development of a real time co-culture monitoring tool.

In summary, this LDRD has been very successful to date, advancing a powerful hyperspectral fluorometric method, establishing capability to cultivate diverse cyanobacteria that can be used as beneficial parts of fuel and/or chemical producing photosynthetic consortia, and producing the discovery of a phototrophic bacterium that exists in co-culture with eukaryotic algae that will result in a submitted paper by the end of the calendar year. These developments have and will support upcoming proposals and future work. The hyperspectral fluorometry technique that this project has developed provides several benefits for algal biofuels work that will strongly position INL relative to others in this field. Our method works with matted biomass and solid phases, and can be used to monitor the biomass production of multiple types of organisms simultaneously at low cost. In addition, our capabilities in maintaining, cultivating, and characterizing cyanobacteria will support an increased variety of biofuels research at INL.
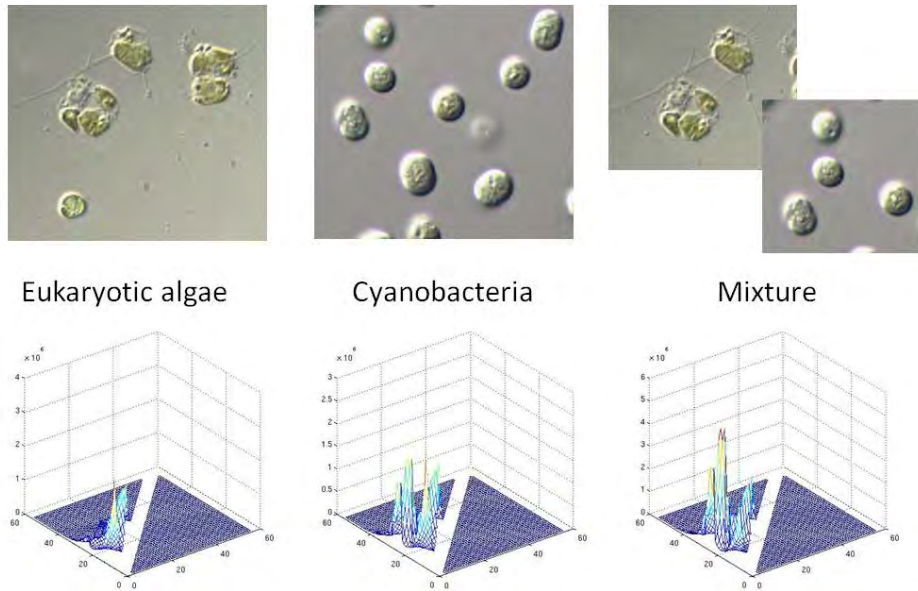
FIGURE 1. Micrographs and hyperspectral fluorescence of single and mixed cultures of algae and cyanobacteria showing difference in spectral features.

Benefits to DOE

The project is aligned with the areas of carbon-to-chemicals, clean water and energy, and bioenergy. Hence, it supports the DOE's energy security mission.

This LDRD will extend INL leadership in the areas of biofeedstock process design, evaluation, and monitoring. It draws on and continues the development of INL strengths in industrial biotechnology, microbial diversity, metagenomics, and chemometrics. In addition, the research supports and develops INL's partnership with Utah State University on large-scale algal production.

Relevant Publications and Presentations

None.

Development of Full-Waveform LiDAR Capabilities for Water Resources and Vegetation Monitoring

Randy Lee and Nancy Glenn[1]

12-101

Two state-of-the-art research applications have been developed with a newly acquired long-range, full-waveform Terrestrial Laser Scanner (TLS): change detection techniques for infrastructure in water resources, and shrub biomass quantification for improved global carbon estimates. These applications demonstrate INL's remote sensing program capabilities in fine-resolution terrestrial and vegetation data collection and modeling.

In regard to the first application, frequent, repeatable data at high resolution are needed to monitor change for a variety of water resource applications. For example, novel and improved methods to monitor changes in structural features of dams and levees may prevent failures, saving lives and resources. Monitoring structural movement and deformation of dams and levees are part of the regular monitoring process to ensure safety and longevity of the structure. Fusion of structural information of a dam/levee (from repeat TLS data scans) provides a unique new understanding of the health of water retention structures, including timely information on size and location of structural defects. The techniques for collecting, analyzing and fusing fine-scale TLS data lend themselves to other water/energy-related challenges.

As for the biomass application, vegetation biomass is important for accurately quantifying biomass production, modeling energy development potential, quantifying fuel loads, and regulatory purposes. Existing methods to quantify vegetation biomass include intensive field destructive techniques that are prohibitive to apply across large DOE installations, due to time and cost.

Summary

Change Detection for Water Resources Infrastructure– Two scans were collected of the Hyrum Dam—a Bureau of Reclamation earthen dam located near Logan, UT (see Figure 1) that has been instrumented with piezometers to monitor for internal moisture in the dam structure. The resulting 3-D point cloud data sets were compared for structural changes or deformation, by creating continuous raster surfaces at the scale of 1 mm per cell, which may indicate change to the internal structure due to leakage in the core of the dam. While there was a measureable amount of change in vegetation on the face of the dam, there was no discernible change in structure of the dam.

Shrub Biomass Quantification for Improved Global Carbon Estimates–In this project, we have developed a method to quantify shrub biomass using TLS and a voxel-based approach. Initial results in comparison to biomass calculated using the traditional field destructive technique are very strong (Figure 2).

In a related study, we developed a method to predict component (leaves and branches) biomass of western juniper using TLS-derived metrics. In this study, a novel method was developed to use the full-waveform capabilities of the TLS to discriminate between the leaves and branches (Figure 3 and Figure 4), whereas in previous studies, these components are combined.

FIGURE 1. 3-D point cloud data and location map of Hyrum dam.
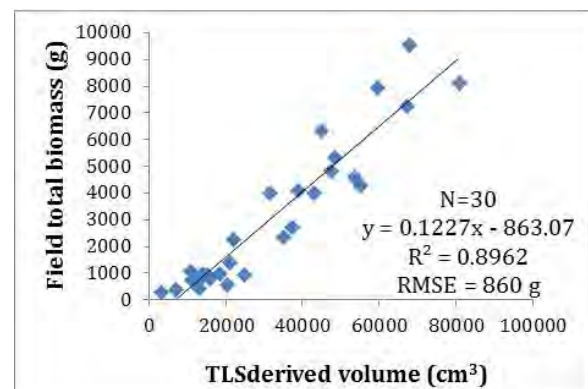
FIGURE 2. Demonstration of the ability to predict sagebrush biomass using TLS -derived metrics. The predicted biomass is the total biomass (green and woody).

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[1] Idaho State University
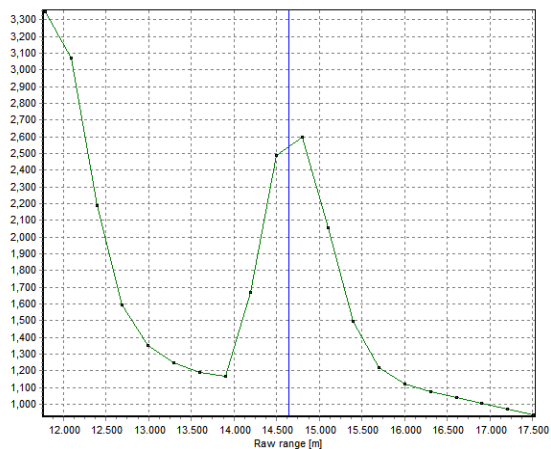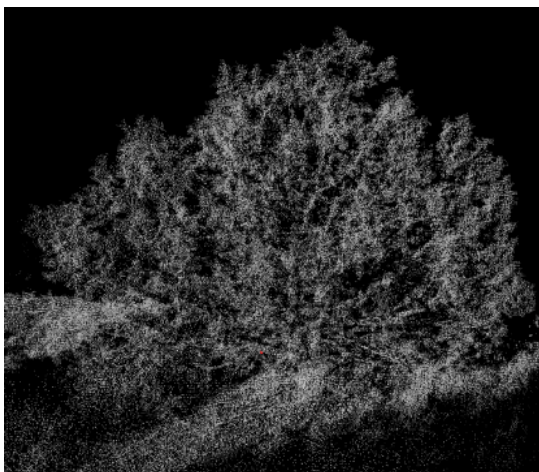
FIGURE 3. TLS point cloud of juniper tree (left) and full-waveform signal used to extract returns for leaves and branches (right).
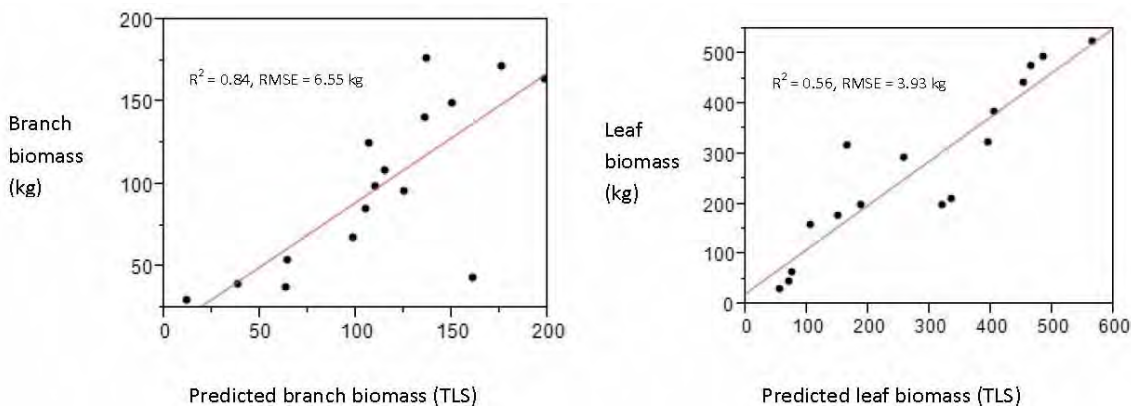
FIGURE 4. TLS-predicted branch (woody) biomass with an R2 of 0.84 (left) and TLS-predicted leaf biomass with an R^2 of 0.56.

This project has partially supported MS student Peter Olsoy's thesis, which he expects to complete and publish in August 2013.

Benefits to DOE

Developing a remote sensing method that accurately quantifies vegetation biomass is beneficial for DOE security missions and for other federal agencies such as the U.S. Department of Agriculture, U.S. Forest Service, and the Bureau of Land Management for fire and restoration

purposes. Furthermore, developing biomass estimates for woody versus green components provides an increased level of accuracy that is needed for biofuel energy estimates. The methods we have developed are applicable to diverse ecosystems, including fluvial and riparian systems.

Knowledge gained during this project provided an estimation of biomass and evaluation and measurement of change on infrastructure benefits environmental quality, energy resources, and basic science. The work that was

performed could benefit a number of federal agencies interested in LiDAR technology.

Relevant Publications and Presentations

We expect to submit one peer-reviewed manuscript in 2012, and a second peer-reviewed manuscript in 2013 on the TLS sagebrush biomass estimations.

Olsoy, P., "Comparison of Biomass Estimation Methods," *Northwest Science Conference, Boise, ID, March 2012*.

Olsoy, P., "Sagebrush Biomass Estimation Using Terrestrial Laser Scanning," *AGU, San Francisco, CA, December 2012*.

Shrestha, R., N. Glenn, L. Spaete, and S. Hardegree, "Above-Ground Component Biomass of Western Junipers Using Full-Waveform and Discrete Terrestrial Laser Scanning," *Silvilaser, Vancouver, BC, September 2012*.

Lower Boise River Water Quality and Natural Resources Management

Mark Ankeny, John Tracy, and Sam Alessi

12-105

Specifically, the objective of this project was to provide the means for Boise, ID stakeholders to compare different strategies for reduction of phosphate loading into the lower Boise River in western Idaho. Generally, such research is important to the nation as a whole to reduce wasted energy and improve water quality in rivers and streams affected by both cities and agriculture.

Summary

We evaluated alternative approaches to phosphate loading in the river from agricultural sources (primarily manure and fertilizer, secondarily food processing waste) and urban sources (primarily waste water from treatment plants and storm water). We also developed an approach to combine both Best Management Practices and performance based payments to land managers (primarily farmers and livestock producers) for water quality improvements.

Informal discussions were made with Idaho Department of Environmental Quality, Idaho Department of Water Resources, Environmental Protection Agency (EPA) Region 10, EPA Office of Water, U.S. Department of Agriculture, and the Cities of Boise, Meridian, Nampa, and Caldwell. We also met with a local fertilizer company and Idaho Power.

Benefits to DOE

This project supports DOE's energy security mission as well as the EPA. Nutrient loading of nitrogen and phosphorus from agriculture to surface water wastes enormous amounts of the fossil-energy expended to produce the nutrients. In addition, the Clean Water Act drives additional monetary and energy expenditures by Total Maximum Daily Load permit holders to remove additional nutrients from waste water to offset agricultural loading.

Relevant Publications and Presentations

None.

Targeted Elimination of Pharmaceutical Compounds from Municipal Wastewater Effluent and Solids

Frank Roberto, Dayna Daubaras, Kara Cafferty, Sandra Fox, and Erik Coats[1]
12-107

Pharmaceuticals and personal care products (PPCPs) are recognized as potentially significant environmental contaminants that can originate from point sources such as municipal waste water treatment plants (WWTPs). While WWTPs are designed and operated to remove most conventional organic and inorganic compounds (e.g., organic carbon, nitrogen, phosphorus) to meet federal water quality permit requirements, treatment facilities are not necessarily functional in removing emerging synthetic compounds such as PPCPs. Nevertheless, improved detection of PPCPs in the environment has been an increasing focus of study over the past decade and there is concern that the long term presence of these compounds in the environment will have profound effects on riparian microorganisms, insects, fish, and humans. To date most research has focused on either assessing the presence of PPCPs in the environment or on developing advanced "add on" technologies for PPCP removal; however, very little attention has been paid to potential treatment within the vast infrastructure of existing WWTPs.

Antibiotics, cholesterol lowering drugs, and antidepressants have been detected in WWTP effluents and downstream bodies of water throughout the U.S. and Europe. Studies suggest that modification of microbial cultures, treatment reactor retention times, or additional post-treatment of sewage solids may improve the degradation of PPCPs prior to release of reclaimed water or solids into the environment. Preventing emission of PPCPs from WWTPs into the environment is an ideal solution to keeping these compounds from entering drinking water supplies. The plan is to mitigate the release of pharmaceutical compounds from the effluent wastewater stream and/or the waste solids of a municipal WWTP by using existing biomass from a functioning WWTP to enrich for microbial consortia capable of degrading target compounds. The target pharmaceutical compounds were selected based on the frequency of use, persistence in the environment, and significant toxicological properties in a human host. Our primary approach is to conduct batch and bioreactor enrichments for microorganisms that may facilitate the degradation of ciprofloxacin, atorvastatin, and carbamazepine. Through adaptation and/or augmentation of actual WWTP microbial samples or effluent streams we will identify conditions for increased efficiency of degradation. The ultimate goal is demonstration of the developed processes within the context of the current design and operating parameters of a functioning WWTP.

A unique component of this work is the ability to directly test promising microbial inocula or modified system parameters in a side-stream of a full-scale operating WWTP at the city of Moscow, Idaho in collaboration with Erik Coats' laboratory at University of Idaho. By studying model compounds in isolation, and adapting and/or augmenting actual WWTP microbial samples, it should be possible to increase the efficiency of pharmaceutical degradation.

Summary

A sensitive detection method to quantify ciprofloxacin, carbamazepine, and atorvastatin from our batch enrichment cultures was established in collaboration with Agilent, using their "RapidFire High-throughput Mass Spectrometry System." Relationships were established with three regional WWTP facilities: Idaho Falls, Rexburg, and Moscow, Idaho. WWTP samples were collected from various treatment areas within the three facilities and approximately 120 enrichment cultures were initiated with varying conditions. Culture enrichments were sequentially transferred and analyzed for pharmaceutical compound degradation for approximately four months. The monitoring of compound degradation by mass spectrometry allowed identification of promising enrichment cultures to be used for enrichments with increasing compound concentrations. Several ciprofloxacin enrichment cultures with greater than 50% compound degradation at elevated compound concentrations were harvested. Carbamazepine enrichment cultures resulted in fewer cultures with approximately 30% degradation. The data analysis for carbamazepine was rather variable, which would require more studies to be conclusive. Several cultures with varying types of microbial growth were considered promising for enhanced degradation of Ciprofloxacin and were stored under long-term storage conditions.

Our collaborators at the University of Idaho completed reactor studies to evaluate pharmaceutical removal in real wastewater treatment environments. Research focused specifically on anaerobic fermentation of raw wastewater, which is a process practiced at full scale wastewater

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[1] University of Idaho

treatment plants that must remove phosphorus from wastewater. The first anaerobic batch experiment was completed at the end of the second quarter 2012 and consisted of four 1-liter reactors that were operated at steady state for 60 days. A second anaerobic experiment was conducted in the third quarter 2012. A third experiment was conducted on the same set of reactors but at a longer solids retention time (SRT; i.e., sludge age). In all experiments, three of the reactors were individually spiked with ciprofloxacin, carbamazepine, or atorvastatin, and a fourth reactor was evaluated as a control. Results from these experiments suggest limited biodegradation potential for any of the compounds in the anaerobic environment. However, significant sorption of ciprofloxacin and limited sorption of atorvastatin was observed. In both cases, however, results suggest that the observed sorbed concentrations were more likely associated with sorption of background levels of the target compounds from long term exposure and not from the spiked fractions. There is a relatively significant temporal difference between hydraulic residence time (HRT) and SRT in the reactors (typical of WWTP operations); in other words the HRT is typically on the order of hours while the SRT is in days. This temporal difference may contribute to the saturation of sorption capacity in the reactor biomass. In addition to these experiments, significant efforts were focused on developing sampling techniques for characterizing removal efficiencies of micro-contaminants in WWTPs. A considerable contribution was made to optimize sample preparation protocols including sorbed fraction "washing" and solid-phase extraction clean-up. Additionally, several analytical approaches were evaluated such as spectrofluorophotometry and gas chromatography with mass spectrometry detection (GC-MS). The GC-MS method was the more promising method.

Benefits to DOE

Water and energy security are integral to one another. Water usage for irrigation, industrial production processes, and urban/municipal purposes requires energy, just as energy production requires water. Water security is vitally important to our Nation's security and thus, protecting our waters from hazardous chemicals protects our water resources. Preventing the release of PPCPs from WWTPs will improve surface and groundwater quality for reuse. Upfront removal of PPCPs before release from WWTPs eliminates the need to research the long-term and complex impacts of PPCPs on the environment and the need for potential cleanup. Developing and demonstrating new strategies to promote biodegradation and reduction of release of PPCPs demonstrates leadership in protecting one of the most valuable resources of our region and nation, water.

Relevant Publications and Presentations

The University of Idaho research group anticipates a publication submitted for peer review in spring 2013.

Cafferty, K.G, D.L. Daubaras, S.L. Fox, E.R. Coats, L.E. Frick, W.A. LaMarr, and F.F. Roberto, "Microbial Degradation of Pharmaceutical Compounds in Municipal Wastewater Effluent," *Mountain West Water Institute (MMWI) workshop "Water Ways & Means," Idaho Falls, ID, May 15, 2012.*

Rehder, R. and E.R. Coats, "Assessing the Practicality of Biological Processes for the Removal of Pharmaceuticals," *The Annual Pacific NW Clean Water Association Meeting, Boise, ID, October 21-24, 2012.*

Bakken Hydraulic Fracturing Water Needs and Potential Impacts to the Fox Hills/Hell Creek Aquifer: A Spatial-Temporal Approach

Thomas Wood, Mitch Plummer, Hai Huang, Luanjing Guo, Jon Reiten,[1] Kevin Chandler,[1] and John Metesh[1]
12-108

One of the most important, rapidly expanding, developments of fossil fuel resources in the U.S. is the Bakken Formation of eastern Montana and western North Dakota. Resource extraction from the Bakken formation relies heavily on hydraulic fracturing (or "fracking") as a means of creating the fracture space needed to promote transport of tightly constrained oil and gas (Figure 1). Fracking requires 2,000,000–5,000,000 gallons of water to fracture one horizontal well. As development of oil and gas in the Bakken formation moves westward, concerns are increasing that artesian aquifers in Eastern Montana, which have historically supported grazing and agriculture, may be impacted. Idaho National Laboratory is partnering with the Montana Bureau of Mines and Geology to perform a water-energy assessment to establish an approach that may be applicable to other developments in the Mountain West with similar water limiting issues.
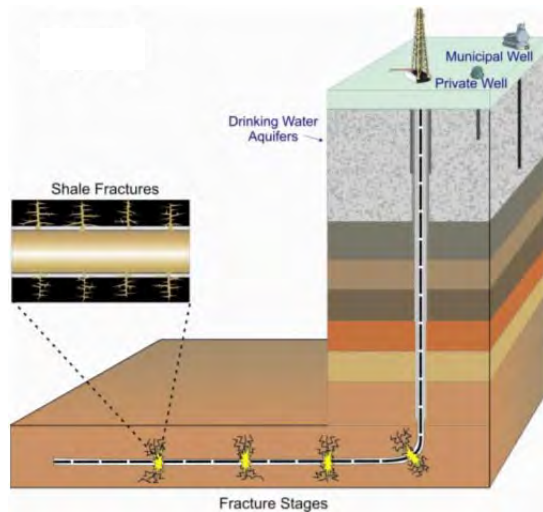
FIGURE 1. Conceptual drawing of an oil well utilizing hydraulic fracturing (from EPA, 2011).

This project is evaluating the water needs for Bakken development in Eastern Montana, characterizing the groundwater resources, identifying key areas where development may be water-limited and developing an approach for optimizing water usage. This research will maximize the energy return on water investment and minimize negative effects. By incorporating the impacts from water consumption into the design of drilling plans through an optimization approach, the negative water impacts associated with energy development can be reduced to manageable levels.

Summary

We assessed the potential water demand for hydraulic fracturing in Montana from studies of similar development in North Dakota. The number of hydraulic fracturing jobs has been increasing. The available data indicate that the amount of water per hydraulic fracturing job has also been increasing. As a result, water demand for energy development in the Williston basin has greatly increased over the last decade. It is likely that a portion of the water for the Bakken development in Montana will be derived from groundwater sources. Our preliminary simulations indicate that the Fox Hills/Hell Creek aquifer may substantially lower water levels in the region. This has been confirmed by water level monitoring by the Montana Bureau of Mines and Geology during FY 2012 (see Figure 2 for a map of the Williston Basin and Bakken Formation).
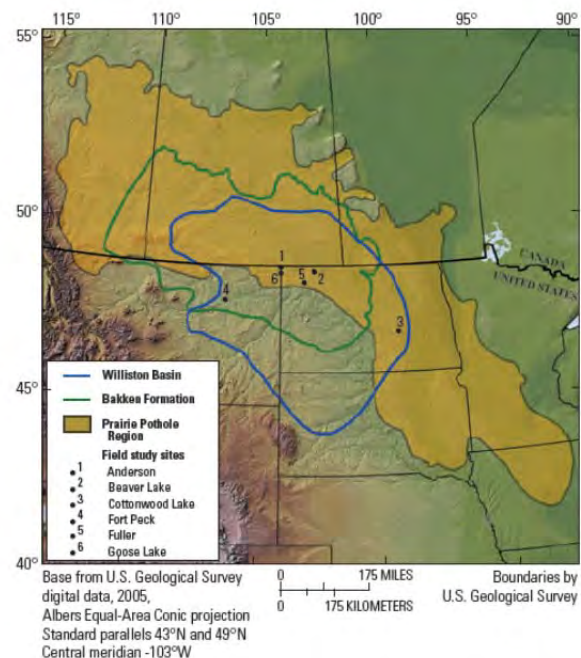
FIGURE 2. Location of the Williston Basin and Bakken Formation (from United States Geological Survey 2011).

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[1] Montana Bureau of Mines and Geology

(a) (b)
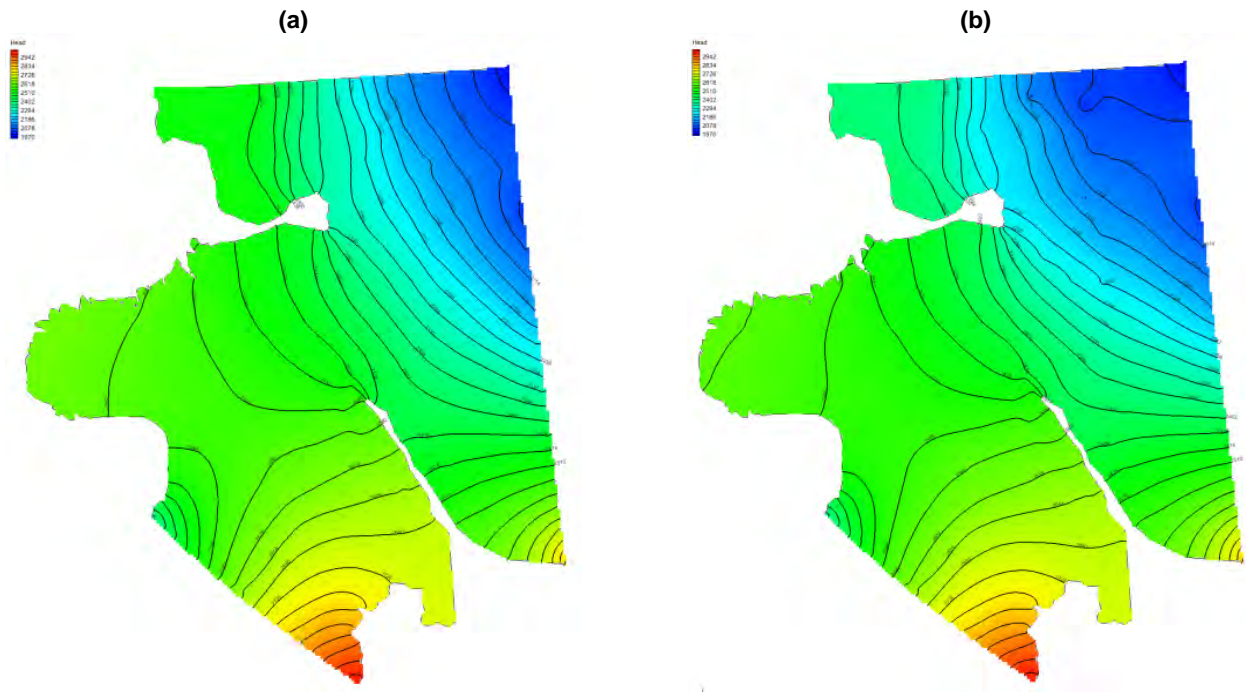
FIGURE 3. Hydraulic head distribution under different discharge scenarios (a) base case; and (b) high discharge scenario for hydrofracing water use.

A conceptual model has been established based on well logs and hydrogeological information on Fox Hill/Hell Creek aquifer and the exchange of data with the U.S. Geological Survey Helena office and North Dakota State Water Commission. A two-dimensional steady state numerical model has been built for the Fox Hills/Hell Creek aquifer based on the conceptual model. The modeling tool we adopted is MODFLOW 2000 embedded in the Groundwater Modeling System. Sensitivity studies have been performed on recharge and discharge. The simulation results of head distribution shown in Figure 3(a) are for a base case steady-state model, and Figure 3(b*)* shows the head distribution with high discharge for equivalent fracking water use (wells pumping at 100 gpm).

Benefits to DOE

Water needed for energy developments throughout the arid Mountain West of North America may limit the nation's ability to address energy security issues. Oil and natural gas from tight sand and shale plays an expanding role in the nation's energy future and hydraulic fracturing is a primary way of accessing these vital resources. Our

research, by focusing on the yet to be developed portion of the Williston Basin in eastern Montana, is at the forefront of development activities that are currently exploding in western North Dakota. We are developing the skills, tools, and resources necessary for these sorts of analyses for energy projects across the arid western states and Canada. Our research will be directly applicable and useful for state and federal agencies evaluating energy development scenarios and land lease sales, aid industry in design of drilling plans and optimizing energy developments to minimize impacts to water resources.

Relevant Publications and Presentations

Reiten, J., K. Chandler, and T.R. Wood, "Watering the Bakken Water Quality and Water Quantity Concerns," *2012 Mountain West Water Institute: Ways and Means Workshop, Idaho Falls, ID, 2012*.

Reiten, J. and J. Thamke, "Energy Development and Water Needs in the Williston Basin," *2012 Montana Section American Water Resources Association, Anaconda, MT, October 11-12, 2012.*

Wood, T.R., L. Guo, H. Huang, M. Plummer, C. Palmer, J. Reiten, and K. Chandler, "Water Needs for Hydro Fracking the Bakken Formation in Eastern Montana – Data Collection and Model Development," *2012 Mountain West Water Institute: Ways and Means Workshop, Idaho Falls, ID, 2012.*

Understanding the Importance of the Role of Soil Moisture Effects for Estimating Snowmelt Runoff in a Mountainous, Snowmelt-Driven Watershed

John Koudelka

12-111

The aim of this project is to improve runoff forecasts from hydrologic models through the use of high performance computing and web-based computational frameworks to improve soil parameter estimation.

Summary

For the first fiscal year of funding, we developed the computational framework that will integrate model components. The web application is being developed in Apache Flex (formerly Adobe Flex), a software development kit for developing and deploying rich internet applications on the Adobe Flash platform. The basemap and spatial data are being served through Economic and Social Research Institute's ArcGIS for Server—a suite of software for disseminating spatial data across the web utilizing web services technology. Since this software was already installed and functioning, this was the preferred choice for serving the geospatial data. ArcGIS for Server supports three Application Programming Interfaces (APIs): JavaScript, Silverlight/WPF, and Flex. The Flex platform was chosen because it is the best supported of the three APIs, the library is more robust and examples are more abundant, the components are more visually appealing, and the Geospatial Science and Engineering personnel have the most experience with it.

Components were developed to connect to model executables that will allow the user to initialize, run the model, and view results. This capability was developed on Robert Jeffers' Water-Energy Spatio-Temporal (known as WEST) hydrologic model to more effectively design the system and get it set for implementation once the model components of this project are ready to be loaded.

One of the most important preprocessing steps is the removal of sinks and pits in the digital elevation model (DEM). In terms of modeling integrity and accuracy, if water cannot flow uninhibited across the surface, then quantities of water are lost, causing error in the calculation of volumes at the watershed outlet. These errors in the DEM need to be removed. The theory of carving an outlet that will essentially remove the pits and sinks by modifying the data, and providing a drain outlet. This technique has not been implemented in parallel before, so a tool was developed over this fiscal year to meet this need. A white paper describing the algorithm is currently being written and will be submitted to a peer-reviewed publication, Environmental Modeling and Software. The algorithm design was presented in poster form at the Spring Runoff Conference at Utah State University in Logan, UT, and the Mountain West Water Institute's annual conference in Idaho Falls, ID.

This work is also supporting the PI's Ph.D. at Utah State University that will be completed in September 2014.

Benefits to DOE

This work supports INL and DOE interests in improving hydrologic modeling accuracy for water resource management and advanced computational modeling capabilities. Water security and management are key components of energy security in the Western United States.

Relevant Publications and Presentations

Koudelka, J.A. and D.G. Tarboton, "A Parallel Algorithm for Removing Spurious Pits from Terrain Data by Carving," *Spring Runoff Conference, Utah State University, Logan, UT, April 2012*.

Koudelka, J.A. and D.G. Tarboton, "A Parallel Algorithm for Removing Spurious Pits from Terrain Data by Carving," *Mountain West Water Institute – Waters of the West Workshop, May 2012*.

Coupled Smoothed Particle Hydrodynamics and Discrete Element Model (SPH-DEM) Simulations of Hydraulic Fracturing and Shale Gas Production

Chuan Lu, Hai Huang, Paul Meakin, Eric Robertson, Milind Deo,[1] Brian McPherson,[1] and Xu Li[2]
12-113

A better understanding of the coupling between fluid flow, deformation, and fracturing in shale formations could increase the gas recovery factor and more adequately address environmental concerns associated with hydraulic fracturing. The overall objective of this project is to develop a physics-based, multi-dimensional, coupled flow-transport-geomechanics/fracturing computer model based on the combination of two particle-based methods (Smoothed Particle Hydrodynamics [SPH] and Discrete Element Method [DEM]). The application of the SPH/DEM model can facilitate systematic studies on the nonlinear interactions/feedbacks between fluid flow, proppant transport and settling, and rock failure and deformation/compaction at multiple scales, ranging from the core/lab scale to the scale of field hydraulic fractures (hundreds of meters). These studies will fill important gaps in knowledge and help provide a fundamental understanding of hydrofracturing.

Technical objectives for this project include: (1) investigate and evaluate SPH-DEM coupling methods, (2) develop a prototype SPH-DEM code coupling fluid injection/flow and rock deformation/fracturing and perform synthetic hypothetic core-scale hydrofracturing simulations, (3) design laboratory core-scale hydrofracturing experiments and conduct preliminary hydrofracturing experiments and imaging analysis of fracture geometries, and (4) prepare manuscripts for peer reviewed journal publications.

Summary

We have developed a parallel DEM code based on MPICH, tested and validated it on multiple platforms. We have conducted preliminary simulations on laboratory-scale tri-axial rock mechanical test. The result was compared with previous results obtained from a DEM code based on OPENMP for validation purposes.

We also developed a serial SPH modeling tool for modeling coupling fluid flow in open space and in porous media, and modeling coupling fluid dynamics and solid mechanics. With this code, we tested some fundamental concepts of using particle methods to describe the interaction of fluid flow and rock deformation in hydrofracturing processes. These concepts include the following aspects.

1. Coupling of fluid flow in open space and porous media is accomplished by using general SPH approach to model fluid flow in open space and explicitly adapt Darcy flow model for porous media. This approach was developed previously for computer graphic illustrations. We have introduced it into the field of hydrology for the first time (to our knowledge) in this work. Figure 1 shows a simulation of an imbibition/drainage process. The initial configuration is shown in Figure 1a. The fluid particle in the void space isolated from outside space is regenerated according to certain rules (Figure 1b). The pressure gradients in a fracture and nearby matrix obey Darcy's law (Figure 1c). The red color indicates solid particles; the blue color indicates fluid particles without mass exchange with solid particles; the green color indicates fluid particles with mass exchange with solid particles.

2. SPH elastic dynamics with tensile failure. The solid elastic dynamics is implemented according to the previous studies in which a rate form of Hook's law is adapted. The tensile failure is modeled by introducing a macroscopic state variable for every solid particle according to the strain history (Grady-kipp model). Figure 2 shows the cracking process of a sample impacted by a plate moving toward left at a constant velocity, several cracks form in the center part of the sample (indicated with red arrows).

3. Coupling of fluid flow and solid elastic dynamics. The interaction between fluid and solid particles is implemented as attractive/repulsive forces according to their distance from what? Figure 3 shows a process of liquid injection into a solid block with a void in the middle. Because of the pressure buildup, the elastic solid container expands and finally breaks. Parameters assigned for the solid properties are closer to rubber, rather than rock, in order to illustrate the deformation processes.

[1] University of Utah

[2] Shell Exploration & Production Company
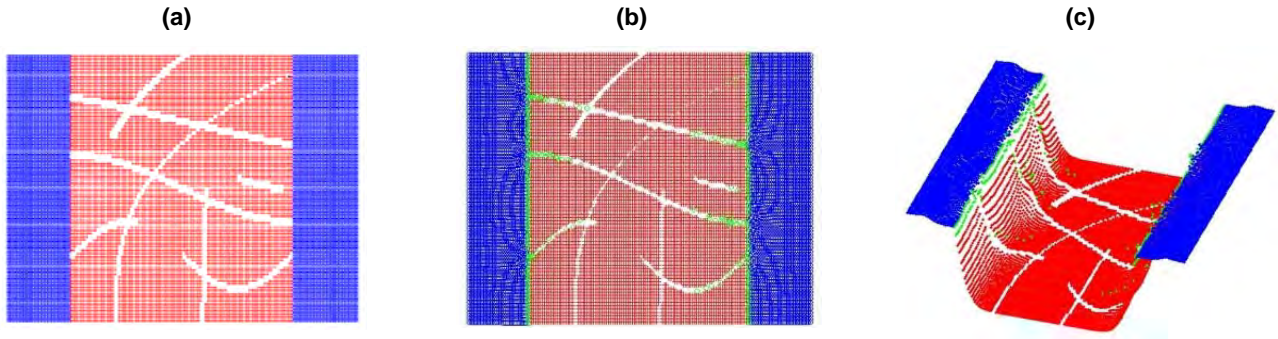
FIGURE 1. Fluid flow in open space and porous media: (a) initial condition; (b) fluid particle position during simulation; and (c) pressure field corresponding to b.
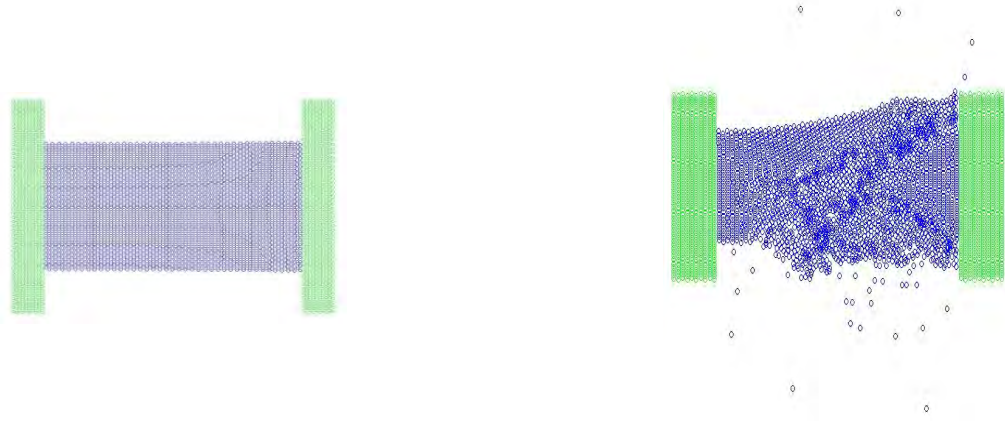
FIGURE 2. Solid sample impacted by object from left. Left panel shows the beginning of contact; right panel shows the cracked sample. Blue circle: sample; Green circle: moving or stationary object.
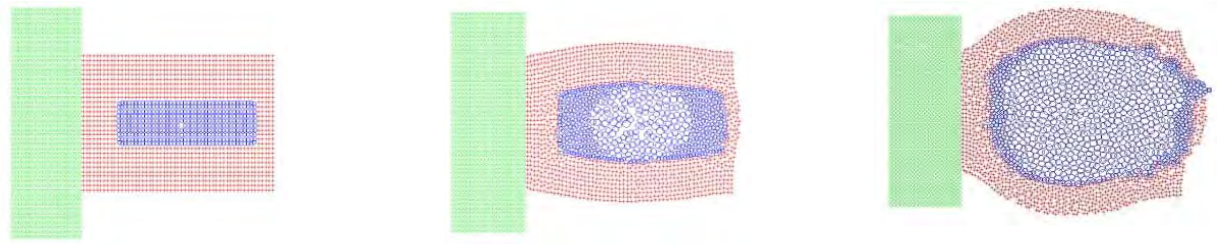
FIGURE 3. Liquid injection into the center of a solid that deforms, expands, and finally fails. The series starts with injection into the initial condition at left, injection continues from center to right where solid fails. Green: stationary object; Red: solid container; Blue: fluid.

We prepared a cement sample for tri-axial hydrofracturing tests and sent it to co-PI, Dr. Mcpherson's laboratory (University of Utah). We inspected all necessary equipment and set up the detailed experimental procedure. Experimental data are expected to be delivered in the next fiscal year. We set up the subcontract with our co-PI, Dr. Deo at the University of Utah. Numerical simulations with the discrete fracture network flow model are ongoing.

Benefits to DOE

This project benefits DOE's mission of energy security as it explores potential improvements in hydrofracturing, a relatively new but increasingly important component of the Nation's energy portfolio.

Relevant Publications and Presentations

None.

A Leap Ahead in Energy Storage: An Integrated Approach to an Inorganic High Energy Lithium Battery

Mason Harrup, Frederick Stewart, Eric Dufek, Aaron Wilson, John Klaehn, and Sergiy Sazhin
12-118

The development of inexpensive and safer energy storage devices is critical to the electrification of the U.S. transport sector. This LDRD project began in FY 2012 with the goal of leveraging DOE's investment and INL's unique niche in high performance hybrid organic-inorganic materials to create an inorganic battery. Several advantages are expected with this concept. First, the use of inorganics—specifically nitrogen (N) and phosphorus (P)—significantly increases the safety of the systems because these materials will not decompose at moderate temperatures (less than 150°C) and they are not flammable. Second, N and P are inexpensive and domestically abundant, which serves to address the nation's energy security. Third, the successful development and deployment of an inorganic battery requires concurrent and closely aligned research efforts to ensure the compatibility of the battery's various components (anode, electrolyte, cathode). DOE's Energy Efficiency and Renewable Energy (EERE) Applied Battery Research (ABR) program has suggested that the concept of the inorganic battery is valid and that the continuation of INL LDRD investment in this project can position INL as a leader in this game-changing revolutionary and essential technology.

Summary

Task objectives were two-fold. First, a new prototype inorganic solvent was to be synthesized and characterized. This was accomplished for the first prototype with very promising results. The viscosity, which was a problem with the previous trimeric phosphazene work, was overcome with the new monomeric solvents. The minimum viscosity achieved with the phosphazenes was 45 cP, which is prohibitively high compared to the alkyl carbonates currently commercially employed, which is 6-9 cP. The first prototype solvent after saturation with the salt ($LiPF_6$) was found to be 9 cP. However, the maximum salt concentration was found to be too low for practical deployment. Therefore, a second prototype solvent was synthesized with alteration to the pendant groups to enhance salt solubility. Characterization work on this second prototype is currently underway.

Second, a new family of advanced lithium salts based upon the oxocarbon anions was to be synthesized and characterized. This was accomplished, but the performance was far below what was anticipated. The

solubility of the salt in a typical blend of alkyl carbonate solvents was found to be 1,000-fold too low to be practical as a lithium ion battery electrolyte. In future years, no more work will be performed on this class of salt. Alternative lithium salts will be investigated instead.

This task directly leverages technology obtained from DOE-sponsored research (ABR program) to expand INL's capabilities in electrode design. Under ABR sponsorship, INL has developed a high energy lithium-ion intercalation anode design that offers many advantages including low cost, safer, and able to function with no appreciable degradation at the 5 volt DOE target for cell performance. Leveraging this technology to develop compatible cathode materials was proposed to further enhance INL's position.

The critical advance for electrode design is the hybrid organic-inorganic scaffold that includes the ability to tailor and engineer the material to enhance and optimize desired properties, such as lithium ion uptake capacity and electrical conductivity. The scaffold also serves as the flame resistant structure by which other additives and can be included to optimize and target performance. The scaffold plays two roles in the electrode. First, it provides structure through which electrons and lithium ions can transport. Second, it actively participates in lithium ion capacity through its nitrogen content.

Significant progress was made during FY 2012 to develop cathode materials based on the scaffold concept. Base polymeric materials were functionalized with groups that can actively engage in lithium-ion oxidation/reduction chemistry. These new materials were characterized using conventional laboratory techniques and will be evaluated electrochemically during FY 2013.

Currently, the activities associated with integrating the new technologies and materials developed so far have been limited due to the early nature of the project. However, all synthetic work has been coordinated by the project team members to consider the requirements and compatibilities between components. For example, a suitable electrolyte cannot dissolve, swell, or negatively interact with an electrode material. As the team moves closer to integrated coin cell testing, closer coordination will be required and resources for this task are planned and accounted for in the out-year budget request.

The expected outcome from this initial investment will take several forms. First, significant Intellectual Property (IP) will be generated. After the IP is secured, the work will be published in peer-reviewed journals, such as Journal of the Electrochemical Society and Journal of Power Sources. Concurrent with publications, presentations will be given at national meetings. Finally, this investment will be leveraged to write proposals to direct funding organizations, such as DOE EERE, Department of Defense, and the private sector that is already in partnership with INL for commercialization of our phosphazene battery technology.

The longer term outcome of this project is the enhancement of the INL's position in a technology for which we are the "go-to" suppliers both in the DOE complex and nationally. The project team and their phosphazene materials are significant capabilities that are unique to INL and make the laboratory the preferred technology provider.

Benefits to DOE

This project could significantly benefit DOE and other relevant agencies. As high energy, portable power sources are in ever increasing demand—both in terms of number of power sources deployed as well as the power desired for each unit—safety and reliability are chief concerns. This new technology could enable a power source based on lithium that has higher voltages, higher total energy density, and superior performance all while being not just safer, but totally safe. Further, this technology could enable a new and improved generation of very large format battery banks capable of supporting a significant increase in intermittent alternative energy utilization (wind, solar, etc.). This is also applicable to grid scale applications that would support infrastructure improvements for more conventional energy sources (coal, gas, nuclear, etc.).

Relevant Publications and Presentations

None.

Modeling-Guided Development of Nanostructured High Energy Electrode Materials for Li-Ion Batteries

Jianguo Yu, Peter Kong, and Michael Glazoff
12-120

Nanostructured electrodes in electrochemical cells have improved conductivity and cyclability performance relative to bulk materials. We are working on a unique science-based strategy, guided by first-principles simulations and thermodynamic modeling of materials, with a goal to screen, plasma synthesize, characterize, fabricate, and test advanced nanostructured high energy electrode materials for Li-ion batteries. Using models accelerates the development of new materials and can help bring new technology to market more quickly. Our ultimate goal is to have an optimized integrated nanostructure basis for cell design, thus using nanomaterials in a way that will greatly improve cell performance, stability, and life-time.

Our objectives for FY 2012 were: (1) Modeling: Investigation of the thermal stability of $LiMn_{1-x}Fe_xPO_4$ at different x values by using a combination of *ab-initio* calculations and statistical mechanical models; and (2) Experiment: Synthesis of nanostructured $LiFePO_4$ using a thermal plasma synthesis process. Concurrently, material structure will be analyzed, the structural and thermal stability of the delithiated $LiFePO_4$ will be characterized, and charge/discharge rate will be tested.

Summary

In the areas of model development we finished the investigation of the thermal stability of $LiMn_{1-x}Fe_xPO_4$ at different x values by using a combination of *ab-initio* calculations and statistical mechanical models. Our results indicated that the thermal stability will be significantly enhanced by doping Fe into $LiMnPO_4$. The stabilized temperatures are 180, 230, and 300°C, corresponding to $LiMnPO_4$, $LiMn_{0.9}Fe_{0.1}PO_4$, and $LiMn_{0.8}Fe_{0.2}PO_4$, respectively.

In addition, to synthesizing anode material SiC, we investigated the relative phase stability of α-SiC and β-SiC by using first-principles atomistic thermodynamics calculations. The calculations suggest that to synthesize α-SiC by plasma, the temperature may need to be higher than 2,650°K. This temperature is easily achievable in thermal plasma.

We also studied the stability of Si_xC_{1-x} by using first-principles calculations, and our results indicate that Si_xC_{1-x} may decompose into C and SiC if x <0.5 Si; Si and SiC if

x > 0.5. These modeling results will provide extra useful information for the following up plasma synthesis process.

In the area of experimentation, we used plasma to synthesize two phases of nanostructured $LiFePO_4$ and $Li_3Fe_2(PO_4)_3$. To test for powder stability in aqueous electrolyte, the plasma generated powder was soaked in water for 24 hours and then dried at 110°C. No change in powder composition was detected after water soaking and elevated temperature drying. This indicates that nanomaterials synthesized by plasma are stable.

We also successfully synthesized a single phase $LiFePO_4$ using conventional solid state reaction with the same reactants as the plasma process with one step. This is a novel accomplishment as the literature reports that $LiFePO_4$ synthesis is a multiple-step process. The solid state reaction condition will be used for the ongoing plasma reactions to produce a single phase nano$LiFePO_4$.

Benefits to DOE

Our project is aligned with DOE energy security missions. An important step for the electrification of the nation's vehicles and for the continued success of the new domestic Li-ion battery manufacturing factories is the development of more cost-effective, long lasting, and abuse-tolerant Li-ion batteries. DOE's continuing investigation into advanced batteries for transportation offers the possibility of reducing green house gases and global warming. The techniques developed here will advance the missions of Basic Energy Sciences, Energy Efficiency and Renewable Energy, and the Office of Vehicle Technology. R&D into advanced batteries for transportation also reduces our dependence on foreign oil and the negative economic impacts of crude oil price fluctuations.

The success of this project will establish a unique experimental, theoretical, and computational capability that will enable acceleration of new advanced materials development and can help bring INL intellectual property to market within a more competitive timeframe.

Relevant Publications and Presentations

None.

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Irradiation-Induced Evolution of Defects and Microstructures in Nanocrystalline BCC Mo

Paul Millett and Yuntian Zhu[1]
10-008

Body-centered-cubic metals, such as ferritic steels and alloys, are used extensively as structural materials in reactor cores. We are developing an atomistic-based knowledge of their deformation behavior both with and without irradiation damage, and with and without helium gas. This research is breaking new ground in this respect, and will enable other scientists and engineers to predict crack initiation and propagation, ductile-to-brittle transitions, and how irradiation and inert gases may accelerate these failure processes. Such a capability will improve the safety and performance of existing nuclear power plants, as well as allow improved material designs for future plants.

To achieve our objectives, we are using both atomistic simulations (molecular dynamics) and experimental techniques (high resolution transmission-electron microscopy [TEM] of helium-ion irradiated samples) to characterize helium bubble formation, and its effect on deformation.

The LDRD supported two postdoctoral associates (one at INL and one at North Carolina State University) to carry out the computational and experimental research.

Summary

We have made significant progress in this research during the project's three-year lifetime. For the computational investigation, Dr. Zhang and Dr. Millett performed an extensive amount of molecular-dynamics simulations to elucidate four primary issues: (1) deformation of un-irradiated nanocrystalline Mo, (2) helium bubble nucleation and growth in the nanocrystalline Mo, (3) dislocation pinning due to helium bubbles, and (4) effect of helium on deformation of nanocrystalline Mo. Our deformation studies revealed that plastic straining predominantly occurs by twinning, and we have found an interesting microcracking mechanism relating to twin-grain boundary intersections. Our helium bubble formation studies yielded very interesting results on the heterogeneous nucleation of helium bubbles, and its dependency on grain boundary type (see Figure 1). Our dislocation/bubble interaction study characterized the dependency of helium bubble pinning force on the bubble's size and gas pressure. Finally, we determined

that helium situated on grain boundaries (GBs) weakens the GBs and leads to earlier cracking in the deformation.
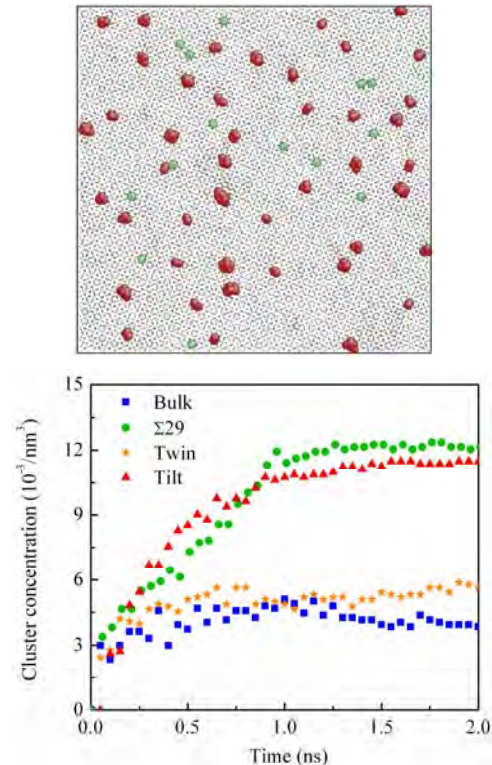
FIGURE 1. Molecular dynamics simulation result showing helium bubble nucleation on a grain boundary plane (top). Helium cluster concentration evolution versus grain boundary type (bottom).

The experimental component of this research has made important progress, although some initial difficulties delayed this work. These difficulties primarily involved an initial inability to fabricate samples with good grain size distributions below 50 nm. However, this has been overcome with the purchase of magnetron sputtering apparatus, and good samples are reliably being produced. In the third year of this project, these samples were irradiated with Helium ions with 200 keV energy, and indentation testing of both irradiated and non-irradiated samples was performed to understand the effect of He bubbles on hardness (which was shown to increase due to the He). TEM observations show He bubble formation on GBs, as shown in Figure 2.

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[1] North Carolina State University
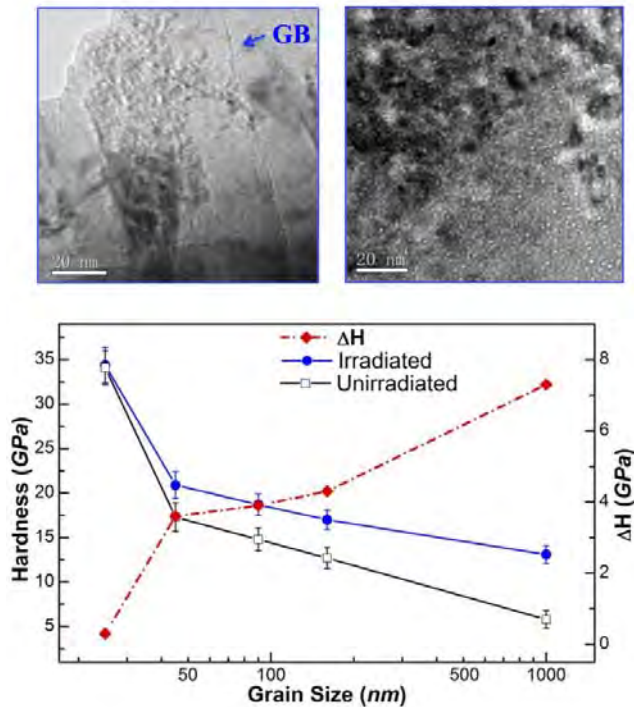
FIGURE 2. High-resolution TEM image of helium bubbles on GBs and in the bulk for He ion-irradiated nanocrystalline Mo (top). The increase in hardness for the irradiated samples, becomes less as the grain size reduces (bottom).

Benefits to DOE

This research contributes to DOE's mission to develop a goal-oriented, science-based approach to understanding and developing nuclear fuels and materials. Insights that will be developed in this project will feed into higher-level modeling and simulation capabilities currently developed at INL, thus providing higher-accuracy, physics-based modeling. As these modeling capabilities improve, the INL will uniquely be able to validate them with experimental comparison enabled by the Advanced Test Reactor, thus solidifying INL's role as the leader in science-based discoveries relating to nuclear materials.

Relevant Publications and Presentations

Cheng, G.M., W.W. Jian, W.Z. Xu, H. Yuan, P.C. Millett, and Y.T. Zhu, "Grain Size Effect on Deformation Mechanisms of Nanocrystalline BCC Metal," Materials Research Letters, 2012. (submitted)

Zhang Y., P.C. Millett, M.R. Tonks, and S.B. Biner, "Deformation Twinning in Nanocrystalline Body-Centered-Cubic Mo by Molecular Dynamics Simulation," *Acta Materialia,* Vol. 60, 6421-6428, 2012.

Zhang Y., P.C. Millett, M.R. Tonks, L. Zhang, and S.B. Biner, "Molecular Dynamics Simulations of He Bubble Nucleation at Grain Boundaries," *Journal of Physics: Condensed Matter,* Vol. 24, 305005, 2012.

Zhang Y., P.C. Millett, M.R. Tonks, and S.B. Biner, "Deformation-Twin-Induced Grain Boundary Failure," *Scripta Materialia*, Vol. 66, 117-120, 2012.

Zhang Y., H. Huang, P.C. Millett, M.R. Tonks, D. Wolf, and D. Phillpot, "Atomistic Study of Grain Boundary Sink Strength Under Prolonged Electron Irradiation," *Journal of Nuclear Materials,* Vol. 422, 69-76, 2012.

Zhang Y., P.C. Millett, and M.R. Tonks, "Energetics and Diffusional Properties of He in BCC Mo: An Empirical Potential for Molecular Dynamics Simulations," *Computational Materials Science,* Vol. 50, 3224-3229, 2012.

Zhang, Y.F., H.C. Huang, P.C. Millett, M.R. Tonks, D. Wolf, and S.R. Phillpot, "Non-Saturable Sinks at Grain Boundaries in Nanocrystalline Mo Under Electron Irradiation," *2010 MRS Fall Meeting, Boston, MA, November 29–December 3, 2010.*

Zhang, Y.F., H.C. Huang, P.C. Millett, M.R. Tonks, D. Wolf, and S.R. Phillpot, "Do Grain Boundaries Saturate in Nanocrystalline Materials-Molecular Dynamics Simulations," *The 2011 TMS Annual Meeting, San Diego, CA, February 27–March 3, 2011.*

Zhang, Y.F., P.C. Millett, M.R. Tonks, and B. Biner, "Deformation Twinning in Nanocrystalline BCC Mo," *MST 2011 Conference, Columbus, OH, October 16-20, 2011.*

Zhang, Y.F., P.C. Millett, M.R. Tonks, L. Zhang, and B. Biner, "He Bubble Nucleation at Grain Boundaries in BCC Mo," *2012 TMS Annual Meeting, Orlando, FL, March 11-15, 2012.*

Zhang, Y.F., P.C. Millett, M.R. Tonks, and B. Biner, "Effect of He Precipitation on the Deformation of Nanocrystalline BCC Mo," *2012 MRS Spring Meeting and Exhibit, San Francisco, CA, April 9–13, 2012.*

Investigation of Molten Bromide Salt Systems for Separation and Recovery of Actinides from Fission Products

Tedd Lister, Prabhat Tripathy, Guy Fredrickson, and Steven Herrmann
10-032

The ability to separate and recover actinides from spent nuclear fuel could not only reduce waste volume but also increase use of nuclear resources across the country. The objective of this research is to investigate the applicability of a bromide-based molten salt system—such as LiBr-KBr and CsBr-LiBr-KBr—to improve the separation and recovery of actinides from fission products in spent fuel. The use of bromide-based salts may introduce three technical benefits over current separation and recovery processes: a lower operating temperature, improved separation of actinides from fission products, and the potential to improve recovery of the actinides by employing bromide electrolysis at the anode.

Summary

Initial work involved performing a literature search on bromide-based molten salt systems as it pertained to electrorefining of used nuclear fuel. This literature search, captured in a report, demonstrated that while some knowledge on the application of bromide salts existed, there was very little on the electrochemistry of elements of interest (actinides and rare earth elements). To perform the experimental work, an electrochemical cell with a furnace provision had to be installed in a new glove box. After the installation was complete, a series of experiments were performed to determine the melting points of three potential molten salt systems:
(1) $LiBr$-$GdBr_3$, (2) $LiBr$-KBr-$GdBr_3$, and (3) $LiBr$-KBr-$CsBr$-$GdBr_3$. Gadolinium was chosen as a surrogate to mimic uranium and plutonium in the electrorefiner. Specific quantities of $GdBr_3$ were added to (1) $LiBr$, (2) $LiBr$-KBr (eutectic composition), and (3) $LiBr$-KBr-$CsBr$ (eutectic compositions) to determine the eutectic melting points/liquidus temperatures of the salt compositions. With increased addition of $GdBr_3$, a corresponding drop in the melting points of the salt compositions was observed. The melting points were lower than the corresponding chloride salt compositions. Electrochemical measurements were performed in the three salt systems. We found that electroreduction of gadolinium, lanthanum, and neodymium could be performed at temperatures as low as $250°C$. Cyclic voltammetry was performed to assess the deposition processes. In some system conditions, the metal deposition process involved multiple steps while others showed just a single reversible deposition step. The stripping of metal deposits (oxidation) was also observed to be reversible with multiple features in some cases. The results are promising in that electrorefining can, in principle, be performed at reduced temperature ($<400°C$) as compared to established chloride systems ($500°C$). A detailed report of the experimental work has been produced as well.

Benefits to DOE

This project helps DOE continue to explore the nuclear fuel cycle and eventually reduce waste. This research expands expertise in the electrochemical treatment of spent nuclear fuels and further establishes the INL as a world leader in innovative fuel cycle technology. This project hired and supported a postdoctoral researcher. The project obtained unique and useful data that could see application to fuel cycle after further evaluations are performed. A significant amount of unique data was obtained which is expected to provide an excellent platform to promote external proposals. The next logical step will perhaps be to engage interested university partner(s) who could continue further studies, particularly applied electrochemical measurements, involving other bromides, possibly via Nuclear Energy University Partnership funding.

Relevant Publications and Presentations

Several papers are planned:

1. Electrochemical Behavior of $GdBr_3$ in Pure LiBr Melt.

2. Electrochemical Behavior of $GdBr_3$ in Eutectic LiBr-KBr Melt.

3. Determination of Electrochemical Window and Electrochemical Behavior of $LaBr_3$ in LiBr-KBr-CsBr Eutectic Melt.

4. On the Binary Phase Diagram of $LiBr$-$GdBr_3$ System.

5. Electrochemical Behavior of $LaBr_3$ in Eutectic LiBr-KBr Melt.

6. Determination of Electrochemical Window and Electrochemical Behavior of $LaBr_3$ in Eutectic LiBr-KBr-CsBr Melt.

7. Electrochemical Behavior of NdBr$_3$ in Eutectic LiBr-KBr Melt.

8. Electrochemical Behavior of NdBr$_3$ in Eutectic LiBr-KBr-CsBr Melt.

Prabhat, K.T., S.D. Herrmann, G.L. Fredrickson, S.X. Li, and T.E. Lister, "Investigation of Fused Bromide Salts for Possible Pyroprocessing Applications," *Institute for Nuclear Energy Science and Technology (INEST) Fuel Cycle Core Outreach and Information Meeting*, *Oregon State University, Corvallis, Oregon, February 21, 2012*.

Microstructural Evolution of UO$_2$ and U Under Irradiation

Maria Okuniewski, Kelvin Lynn,[1] Marc Weber,[1] Kasey Lund,[1] Douglas Akers, Craig Shull, Mark Drigert, and Lyle Roybal

10-058

Positron annihilation spectroscopy is a non-destructive technique that is sensitive to open volume defects, such as vacancies, voids, and dislocations. Hence, this technique is optimal for examining irradiation damage in materials. The objective of this proposed research was to elucidate the microstructural evolution in irradiated uranium-(U) based alloys with positron annihilation spectroscopy (PAS) and transmission electron microscopy (TEM). Moreover, a new reconfigurable PAS system was developed to analyze irradiated materials. The results from the PAS and TEM can be used to understand the microstructural evolution in U alloys as a function of various irradiation parameters, such as dose and temperature. PAS and TEM are utilized to analyze defects and to determine defect energies in U alloys. Since PAS is relatively insensitive to defects greater than 1 nm, TEM was selected to qualify and quantify defects greater than 1 nm. Metallic U-based alloys were focused on since they are model fuels for fast reactors. The significance of this research is that it provided unique data; crucial input and validation data for a multi-scale, multi-physics model; a new PAS experimental system; and can eventually lead to a better understanding of the impact of microstructure on the thermal and mechanical properties of fuels.

Summary

To achieve the project's goals, a three-pronged approach was established: (1) U-based alloys were fabricated and characterized. These materials were then irradiated to low fluences. Following the irradiations, the alloys are pending PAS and TEM analyses. These experiments will provide information related to the microstructural evolution. (2) In situ heating experiments were performed with U while conducting simultaneous positron annihilation measurements on the PAS beamline at Washington State University. The objective of these experiments was to determine the defect energies in U alloys, which are a crucial link to modeling and simulation. (3) A re-configurable PAS system was designed, built, tested, and deployed for the analyses of irradiated materials. This system is important for analyzing irradiation induced defects.

In order to obtain the defect data of interest, first a variety of polycrystalline U-based alloys (pure depleted U or DU, DU-Zr, and DU-Mo) were fabricated to examine the differences in irradiation damage with respect to PAS and TEM. Chemical analyses, microscopy, PAS, and synchrotron x-ray diffraction were performed on all of the as-cast alloys to serve as a control prior to irradiation. An example of the TEM results from a DU-Zr alloy is shown in Figure 1(a).

Experiments were also conducted to examine the microstructural evolution of unirradiated U as a function of temperature with the Doppler broadening PAS technique to determine defect energies, such as the vacancy formation energy. The in situ, temperature controlled PAS experiments were carried out on the positron beamline at Washington State University. Defect energies are necessary for the accurate parameterization of computational models. The results from one of the in situ experiments are shown in Figure 1(b), which indicates the S parameter response as a function of temperature in U. These in situ PAS studies were found to agree reasonably well with recent first principles simulations conducted by others in the industry.

The final component of this research was a re-configurable PAS system to analyze irradiated materials, which was designed, built, tested, and deployed. This re-configurable PAS system, as shown in Figure 1(c), has the capabilities of conducting both Doppler broadening, coincident Doppler broadening, and lifetime measurements. This system was designed with a data acquisition system, the capability to spatially resolve components in the x and y directions, and a user-friendly interface. This system is now located in the CAES building and is anticipated to become part of the suite of instrumentation that is utilized by the ATR-NSUF researchers, as well as others that may benefit from PAS analyses.

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[1] Washington State University
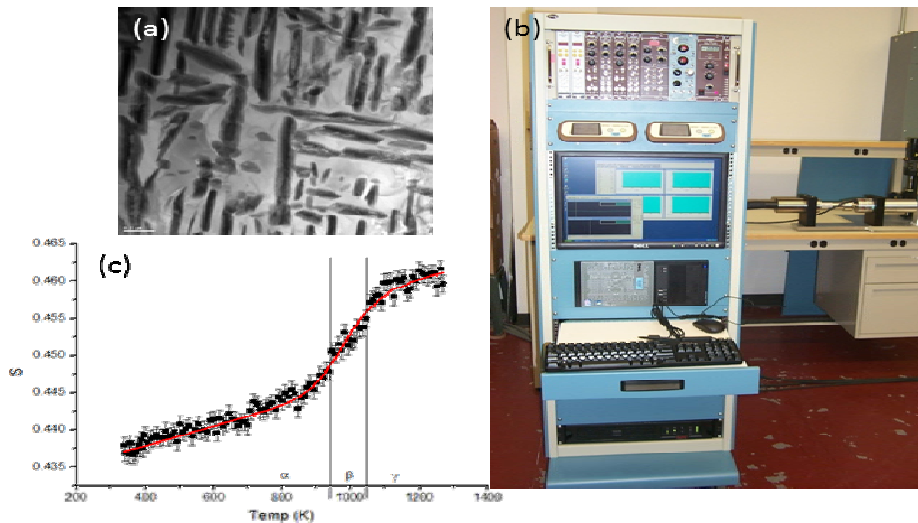
FIGURE 1. (a) TEM micrograph of U-10wt%Zr alloy. (b) Re-configurable PAS system with the high purity germanium detectors shown in the background. (c) S parameter response as a function of temperature in metallic U.

Benefits to DOE

This research has benefited the DOE national security mission through the design of a unique PAS to analyze radioactive materials. This non-destructive PAS system can also be applied to a wide variety of materials other than nuclear, such as fuel cells, semiconductors, plastics, and batteries, hence enhancing the experimental capabilities crosscutting throughout many DOE missions. Moreover, this research has provided defect energetics necessary for the parameterization of models. Ultimately, the microstructural evolution data will be utilized to validate the multi-scale, multi-physics models.

Relevant Publications and Presentations

Lund, K.R., K.G. Lynn, M.H. Weber, and M.A. Okuniewski, "Vacancy Formation in Polycrystalline Depleted Uranium," *Proceedings of the 16th International Conference on Positron Annihilation (ICPA-16), Bristol, United Kingdom, August 2012.* (Accepted for publication in Journal of Physics: Conference Series.)

Okuniewski, M.A., M.H. Weber, K.G. Lynn, B.W. Beeler, B.J. Good, C.S. Deo, M.I. Baskes, S.A. Maloy, and J.F. Stubbins, "Positron Annihilation Spectroscopy in Nuclear Structural Materials and Fuels," *The Twelfth International Workshop on Slow Positron Beam Techniques, Magnetic Island, Australia, August 2010.*

Okuniewski, M.A., "Microstructural Evolution in Nuclear Fuels: Connecting Experiments and Simulations," *Idaho National Laboratory presentation for Secretary of Energy, Dr. Steven Chu, Idaho Falls, ID, September 2010.*

Okuniewski, M.A., "Microstructural Evolution in Nuclear Fuels: Connecting Experiments and Simulations," *Idaho National Laboratory presentation for Under Secretary of Energy, Dr. Arun Majumdar, Idaho Falls, ID, January 2012.*

Okuniewski, M.A., "Positron Annihilation Spectroscopy in Nuclear Fuels and Materials," *Idaho State University, Nuclear Engineering Colloquium, February 2012.* (invited)

Okuniewski, M.A., D.W. Akers, M.W. Drigert, C.L. Shull, and L.G. Roybal, "Spatially Resolved Positron Annihilation Spectroscopy in Nuclear Fuels," *American Nuclear Society Meeting, Chicago, IL, June 2012.*

Okuniewski, M.A., D.W. Akers, M.W. Drigert, C.L. Shull, and L.G. Roybal, "Spatially Resolved Positron Annihilation Spectroscopy in Nuclear Fuels," *16th International Conference on Positron Annihilation (ICPA-16), Bristol, United Kingdom, August 2012.*

173

Design and Testing of a Mars Hopper

James O'Brien, Nathan Jerred, Robert O'Brien, and Steven Howe

10-081

This project supported the development of a prototype Mars Hopper test rig. A Mars Hopper is an instrumented platform to be placed on the surface of Mars, designed to acquire highly detailed data from the surface and subsurface, travel large distances to multiple sites in short periods of time, and perform this task repeatedly. Objectives for the FY 2012 portion of this project included design, fabrication, and testing of a laboratory-scale prototype of the Hopper heated core. In the prototype, core heating is provided by electrical heater rods, simulating radioisotope decay heat. The prototype was designed for carbon dioxide (CO_2) flow through the heated core. Flow and temperature instrumentation provide validation data for comparison to previously completed computational simulations.

Summary

Under this project, a laboratory-scale test rig was developed to provide benchmark data for comparison to simulations. With empirical data, both computational fluid dynamics and thermal hydraulic codes can be validated, allowing for design iterations to be performed numerically to fine-tune the probe design and ultimately maximize its performance. The test rig utilized two plenums for gas injection and exhaust handling. The entire inner assembly was encased within a titanium shell that contains both the radial insulation scheme and the inner core. At the center of the core is a 275 W electric heater that simulates radioisotope heat. Zirconia disks were used to thermally isolate the core axially from the injection and exhaust plenums. Tie rods (connected to flanges fitted to each plenum) were used to axially compress the entire test rig through thermal cycling and blow-down testing. Investigators considered several initial design concepts for the test rig's inner core. This process led to the selection of bundled rods, reminiscent of nuclear test reactor hexagonal-based cores. This configuration was determined to be best suited from both a fabrication and materials handling perspective.

Investigators pursued two rod designs that produce two unique inner core assembly and flow channel geometries: (1) circular rods; and (2) a hexagonal-based design. The

heater rod is at the center of the inner assemblies. The rod is encased in a Hastelloy C-276 shell designed to fit in the respective assembly. In order to radially contain the inner bundled rods, a Hastelloy C-276 outer shell was used for each respective design. Heater rods were fabricated from Hastelloy C-276 as a surrogate for beryllium rods. The current project work scope included thermal cycling of the prototype to test its structural integrity and to perform preliminary blow-down testing with CO_2 gas to better understand the test rig's performance and finalize its overall design. The test apparatus is primarily comprised of a pressure vessel designed to hold the Hopper prototype for testing. The pressure vessel simulates Martian ambient conditions such as providing a rough vacuum of 1000 Pa (0.01 atm) with a CO_2 atmosphere. Additionally, the vessel also acts as an engineered safety control in the event of a failed blow-down test. A pressurized train was integrated with the test rig to safely inject as well as handle the hot CO_2 gas.

A mass flow meter and variable-area flow valve are located upstream of the test rig to control and monitor gas flow rates through the prototype. Hot gas exits the test rig through a finned-tube heat exchanger where it is cooled prior to flowing into the general laboratory exhaust system. The test rig itself has been fitted with various thermocouples in order to monitor the inner core temperature at several axial positions, provide feedback control for the heater and to monitor the outer shell temperature throughout each experiment. Gas pressure data is gathered via an upstream pressure transducer, as well as a differential pressure transducer, measuring the pressure drop across the core. Additionally, gas temperatures are measured upstream and downstream of the heated rig. The pressure vessel itself has a double-walled design with constant wall cooling provided by a continuous flow of water. To ensure inner wall temperature limits of the vessel are not exceeded, a thermocouple is also attached directly adjacent to the test rig. A photograph of the test rig is presented in Figure 1.
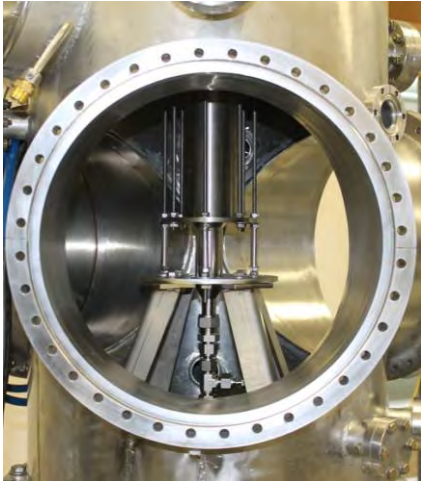
FIGURE 1. Hopper prototype test rig assembled and mounted in the pressure vessel.

Benefits to DOE

Performance requirements for NASA planetary exploration missions are increasing. Landing at a single location to take data is no longer sufficient and due to the increasing cost, the missions that provide mobile platforms that can acquire data at displaced locations are becoming more attractive. This program is designing an instrumented platform that can acquire detailed data at hundreds of locations during its lifetime—a Mars Hopper. The platform will be able to "hop" from one location to the next every 5–7 days. Several platforms may be deployed on a single launch from Earth, and with a lifetime estimate of 5 to 7 years, the entire surface of Mars could be mapped in detail by several platforms. Furthermore, the basic platform can be deployed to Europa, Titan, and even Venus with minor alterations. More ambitious technologies and scientific methods must be developed to increase the science return for each launch, thus increasing the scientific value for the money spent for each mission. Several previous studies have proposed the use of "hoppers" powered by various means. However, these concepts suffered from both short range and relatively short operational durations. Conceivably, if an instrumented platform could be placed on the surface of a planet, highly detailed data could be acquired.

Relevant Publications and Presentations

Jerred, N.D., W.S. Cooley, R.C. O'Brien, S.D. Howe, and J.E. O'Brien, "The Mars Hopper: Development, Simulation and Experimental Validation of a Radioisotope Exploration Probe for the Martian Surface," *AIAA Space 2012 Conference and Exposition, Pasadena, CA, September 11-13, 2012*.

Howe, S.D., R.C. O'Brien, R.M. Ambrosi, B. Gross, J. Katalenich, L. Sailer, M. McKay, J.C. Bridges, and N.P. Bannister, "The Mars Hopper: An Impulse-Driven, Long-Range, Long-Lived Mobile Platform Utilizing In-situ Martian Resources," *Acta Astronautica*, Vol. 69, 1050-1056, 2011.

O'Brien, R.C., A.C. Klein, W.T. Taitano, J. Gibson, B. Myers, and S.D. Howe, "Thermal-Hydraulics of a Radioisotope-Powered Mars Hopper Propulsion System," *Nuclear and Emerging Technologies for Space, Albuquerque, NM, 2011*.

O'Brien, R.C., N.D. Jerred, and S.D. Howe, "Development of a Propulsion System and Component Test Facility for Advanced Radioisotope Powered Mars Hopper Platforms," *Nuclear and Emerging Technologies for Space, Albuquerque, NM, 2011*.

Howe, S.D., R.C. O'Brien, W.T. Taitano, D. Crawford, N. Jerred, S. Cooley, J. Crepeau, S. Hansen, A. Klein, and J. Werner, "The Mars Hopper: a Radioisotope Powered, Impulse Driven, Long-Range, Mobile Platform for Exploration of Mars," *Nuclear and Emerging Technologies for Space, Albuquerque, NM, 2011*.

Jerred, N.D., R.C. O'Brien, S.D. Howe, and J.E. O'Brien, "Development of the Variable-Atmosphere Testing Facility for Blow-Down Analysis of the Mars Hopper Prototype," *Nuclear and Emerging Technologies for Space, Albuquerque, NM, February 25-28, 2013*.

Jerred, N.D., W.S. Cooley, R.C. O'Brien, S.D. Howe, and J.E. O'Brien, "The Mars Hopper: Development, Simulation and Experimental Validation of a Radioisotope Exploration Probe for the Martian Surface," *AIAA Space 2012 Conference and Exposition, Pasadena, CA, September 11-13, 2012*.

In Situ Characterization of an Oxide Film for Prediction of Stress Corrosion Cracking Susceptibility

Sebastien Teysseyre, David Hurley, Zhandes Utegulov, and Tedd Lister
10-083

Stress corrosion cracking is an obstacle for extending the life of nuclear power plants and designing materials for the next generation of such plants. It is believed that changes in the oxide layer composition are linked to stress corrosion cracking initiation, that the efficiency of the mitigation techniques, and the long-term influence of a temporary loss of water chemistry control on stress corrosion cracking initiation can be determined by in situ characterization of such changes. This project is developing a corrosion loop with the capability to characterize, in situ, the response of an oxide film to water chemistry changes and to stress in boiling water reactor and pressurized water reactor environments using Raman spectroscopy, laser ultrasonics, and electrochemical impedance spectroscopy. In addition, the feasibility of using laser ultrasonics to determine the thickness and elastic mechanical properties of the oxide film was determined.

Summary

So far, we have developed the apparatus to perform in situ measurement in boiling water reactors or pressurized water reactors environments (further description of the apparatus is below). Raman spectroscopy and electrochemical spectroscopy data were produced in various environments. The feasibility study of using laser ultrasonic in water showed that water introduces an additional complexity in analyzing the data and that such an approach will require a significant amount of work to be available in the context of this research project.

The testing facility consists of a closed-loop flowing water system. For ultimate control of water chemistry, the loop is built out of titanium, although some parts at room temperature and atmospheric pressure have polytetrafluoroethylene fittings. The water chemistry is first prepared and controlled using a water board where pure water is stored in a glass column. Gas is bubbled through the columns and a small positive gas pressure can be applied in order to control the dissolved gas content of the water. The column is connected to a recirculation loop that directs the water through an ion exchanger, if needed, to maintain purity. A conductivity meter was installed in the recirculation loop to permit continuous monitoring of the water conductivity at room temperature and atmospheric pressure. When the desired conditions are reached, the water is pressurized and heated up to a temperature close to the target temperature before it flows into the autoclave. A high-pressure pump pushes the water from the column to the autoclave through the preheater and controls the flow rate for the experiment up to 200 ml/min. The pressurized water is heated to a value that is close to the testing temperature by flowing through a regenerative heat exchanger and preheater. Once inside the autoclave, the water is maintained at the desired temperature by a heating band clamped to the autoclave body, and an insulating jacket. The temperature is measured by a thermocouple located inside the autoclave. After flowing through the autoclave, the water is cooled down to room temperature before it returns to the water board. The water goes through a back pressure regulator (BPR) where the pressure is reduced. After the BPR, the water is at atmospheric pressure and flows through a conductivity meter before returning to the primary column.

The autoclave is titanium built, rated up to pressurized water reactors conditions and equipped with a sapphire window that allows use of laser based techniques. The main challenges were to be able to seal the autoclave and align the specimen with the laser beam. The current design allows insertion of specimens without breaking the seal, and allows the operator to bring the specimen in focus with the laser beam. Two specimen holders were designed and built: one for corrosion exposure; and one that allows loading the specimen using a 3-point bending technique. A glass cell has been designed and built. This cell is suitable for low pressure type testing for the study of the evolution of the oxide layer of zirconium 4 once in contact with low temperature chloride environment.

Use of electrochemical impedance spectroscopy and raman spectroscopy. Zircalloy 4 was oxidized in air at 550^0C then immersed in a de-aerated solution of 1 M hydrochloric acid (HCl) at 90^0C. Addition of either copper chloride ($CuCl_2$) or iron chloride ($FeCl_3$) was performed in order to destabilize the surface film. Electrochemical potential reading and electrochemical impedance spectroscopy were used to detect the perturbation of the oxide film. The result was compared to Raman spectroscopy measurements. Results suggest that the oxide film was destabilized and corrosion pitting occurred; Raman spectroscopy did detect a change in the oxide with a shift of the peak present at 279 cm^{-1}. The meaning of the disappearance of this peak alone is still under investigation.

Raman spectroscopy readings. In this work, alloy X750 exposed to a boiling water reactor environment was used for Raman readings. Readings are compared to known oxide powders (magnetite [Fe_3O_4], nickel chromate [$NiCrO_4$], nickel iron oxide [$NiFe_2O_4$]) and literature data. All readings are consistent with the literature.

Benefits to DOE

Stress corrosion cracking and irradiation stress corrosion cracking are phenomena that challenge the integrity of our nuclear power plants. Therefore, they challenge the capability of the U.S. to extend the lifetime of the current fleet, impose down times that increase the cost of energy production, and raise concern for the design of next generation of nuclear reactors.

This work, along with the equipment developed, will help studying stress corrosion cracking mitigation techniques and predict the deleterious effect of chemistry changes in the operation of a nuclear power plant.

Relevant Publications and Presentations

Teysseyre, S., M. Khafizov, D. Hurley, and T. Lister, "Development of Laser Based Techniques for In situ Detection of Environmentally Assisted Degradation of Materials," *The International BWR and PWR Materials Reliability Program Conference and Exhibition, July 16-19, 2012.*

Supercritical Fluid Extraction of Actinides from TRISO Reactor Fuels

Bruce Mincher and Chien Wai[1]
11-006

Very High Temperature Reactors are a high priority concept for new reactor design. They rely on tristructural isotropic (TRISO) fuels, in which the UO_2 fuel is encapsulated in layers of pyrolytic graphite and silicon carbide. These refractory materials prevent conventional dissolution of used TRISO fuels prior to any reprocessing scheme developed to recover uranium. Supercritical fluid extraction (SFE) is a technique that facilitates the extraction of uranium or other desired constituents from solid or porous matrices without the need for conventional acid dissolution. The utility of the technique is proven, and it is currently used to recover uranium from solid waste at an AREVA facility in the state of Washington.

The question we are addressing with this project is, "Does SFE have advantages for the recovery of uranium and/or other actinides from TRISO fuels?" Toward this end, we have investigated the extraction of uranium, neptunium, and plutonium from TRISO fuel and from acidic solution using a $TBP•HNO_3$ complex in supercritical CO_2. If actinide extraction is found to be efficient, and if separations chemistry is possible in this medium, then the advantages of the approach would include the absence of a need for handling crushed irradiated fuels, the absence of an acid dissolution step, and the absence of bulk amounts of organic solvents as are disadvantages in conventional liquid/liquid solvent extraction.

Summary

Significant progress has been made on two fronts. First, a method has been devised that allows in situ fracturing of the refractory graphite and silicon carbide coatings of TRISO fuel particles. This is performed in the same vessel that is then used for the SFE. Thus, all the fuel dust and fission products, including volatile fission products, associated with irradiated fuel would be totally contained during supercritical fluid processing.

Secondly, we have begun to develop separations chemistry in supercritical carbon dioxide for uranium/neptunium and plutonium partitioning. We quickly determined that the $TBP•HNO_3$ complex is oxidizing toward the actinides so that when the ligand is deposited directly on to the material to be extracted, all the metals are converted to their higher oxidation states. This initially suggested that no separations chemistry would be

possible. However, we found that if the $TBP•HNO_3$ complex is first dissolved in supercritical CO_2 it is not as strong an oxidizer. For example, we were able to extract uranium as UVI, while the use of acetohydroxamic acid (AHA) complexed and prevented PuIV and NpIV/V extraction under moderately acidic conditions. Oxalic acid also prevented PuIV extraction, as shown in Figure 1. On the other hand, the use of 20 mM sodium nitrite was insufficient to reduce neptunium to NpV, suggesting that SFE is still more oxidizing than similar liquid/liquid extractions.
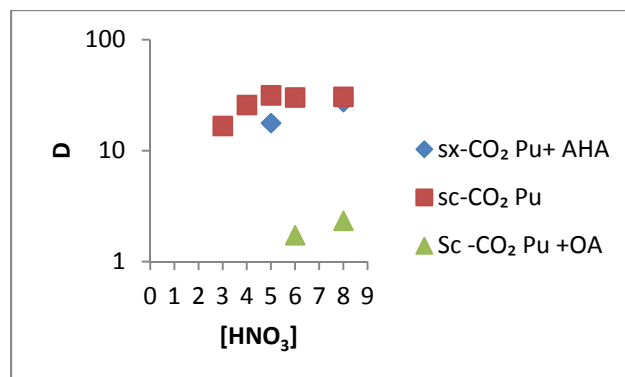
FIGURE 1. The SFE extraction of plutonium (squares), plutonium in the presence of AHA (diamonds) and plutonium in the presence of oxalic acid (triangles).

Benefits to DOE

The success of this project contributes to the potential for reprocessing of used TRISO fuel—a key component of DOE's work in the next generation of nuclear reactors. Although this fuel has received much attention for the development of fast reactors, there has been almost no work done until now regarding its post-burn-up treatment. The invention of a total containment method during fracturing of the refractory coating and the selective extraction of uranium in the presence of the other actinides are necessary steps toward the eventual efficient utilization of TRISO fuels. Additionally, the project has contributed toward the continued development of both separations and SFE expertise at INL. The combination of these two technologies at INL is fitting since the use of SFE in metal extraction is a University of Idaho invention,

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[1] University of Idaho

and its development for nuclear applications by INL is especially satisfying. Further, the project is helping to train the next generation of nuclear scientists, with a Ph.D. candidate performing the work in fulfillment of her dissertation requirements.

Relevant Publications and Presentations

Quach, D.L., B.J. Mincher, and C.M. Wai, "Supercritical Fluid Extraction and Separation of Actinides," *FCR&D peer review meeting, Idaho Falls, ID, June 19, 2012*.

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Wai, C.M., D.L. Quach, Y-J. Liao, and B.J. Mincher, "Separation of Uranium from Actinides and Lanthanides in Supercritical Fluid Carbon Dioxide," *American Chemical Society Northwest Regional Meeting, (NORM) 2012, Boise, ID, June 14–27, 2012.*

In-Situ Micro-Raman Spectroscopy and Modeling of Breakaway Oxidation of Zircaloy Cladding

Marat Khafizov, Asle Zaeem, Mahmood Mamivand, and Haitham El Kadiri[1]
11-041

Thermally-grown oxide scale on zircaloy acts as a protective layer for further oxidation of the metal. Past research into Nuclear Reactor materials has suggested that crack development in TGO scale due to internal stresses has strong detrimental effects on the adherence and protectiveness of the TGO coating and thus, drives breakaway oxidation. Cracks may induce the layer to spall off, allowing hydrogen to easily penetrate and reach the metal, thereby forming brittle hydrides and reducing the adherence of the TGO.

The overarching goal of this project is to predict the threshold of breakaway oxidation for zircaloy-4. Fundamental gaps forestall the development of predictive models, which has motivated the research objectives of this project. Gaps reside in the understanding and modeling of stress generation and crack patterning in the oxide scale and in their relation to the kinetics and transformation in the oxide layer.

Originally, this project was launched based on the widely admitted hypothesis that breakaway oxidation is *directly* associated with the scale deterioration due to tetragonal-to-monoclinic transformation stresses and oxidation stresses. However, in addition to Micro-Raman spectroscopy and phase field (PF) modeling, extra experimental and modeling efforts were performed at Mississippi State University during year one and even more substantially in year two. These included use of atomic force microscopy (AFM), optical microscopy, and Eshleby's based micromechanical calculations. These techniques revealed that breakaway oxidation is due to the change of the sign of circumferential stress from compressive to tensile at the free surface of the oxide scale. This tensile stress triggers radial cracks that catastrophically propagate toward the interface. Thus, corrosive elements such as oxygen and hydrogen penetrate the oxide scale and thereby reach the metallic substrate.

The evolution of the circumferential stress $\sigma_{\theta\theta}$ is given by Equation (1) under small strain assumptions. This stress at a point (r) in the oxide scale from the interface, mainly depends on the variation of the circumferential stress at the interface ($\sigma_{\theta\theta}^i$), oxidation thickness (h), and radius of the interfacial imperfection (R):

$$\sigma_{\theta\theta} = \sigma_{\theta\theta}^i + \frac{2E(m-1)}{3(1-\upsilon)m}\left[\frac{r}{R} - \left(1 - \frac{h}{R}\right)\right] \tag{1}$$

where

  m = ratio of the new volume of zirconium oxide to the consumed zirconium volume

  E = Young's modulus

  υ = Poisson's ratio.

To obtain the three above variables, the following PF models are being developed:

1. (Model 1) Stress dependent oxidation model responsible for stress generation in the metal and oxide scale. This PF model is necessary to provide h and also part of $\sigma_{\theta\theta}^i$. Model 1 was developed in years one and two.

2. (Model 2) Stress dependent PF model for phase transformation from tetragonal to monoclinic transformation. This Model 2 is necessary to compute the final evolution of $\sigma_{\theta\theta}^i$, and was developed in year two. In addition, a precipitation model (Model 0) was developed in year one.

3. (Model 3) Stress dependent PF model for interfacial roughening due to the biaxial oxidation stresses (Model 1) and phase transformation stresses (Model 2). This Model will be developed in year three.

4. A coupled PF model between the above three PF models. This will be compiled in year three.

These mechanisms have never been addressed in the literature, which helps explain why breakaway oxidation has not been understood and predicted.

Summary

The major research objective in year two was to develop the model for the tetragonal-monoclinic transformation (Model 2 above). This transformation impacts thermal barrier coating techniques as well as nuclear fuel performance modeling. This PF model was developed based on the martensitic twinning mechanisms previously identified in the literature via transmission electron microscopy (TEM) and AFM analyses. This task was successful as we reproduced the experimental results of the kinetics and morphologies reported in the literature. Figure 1 provides a comparison of monoclinic twins in a tetragonal matrix between our PF simulation results and TEM results reported in the literature.

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[1] Mississippi State University
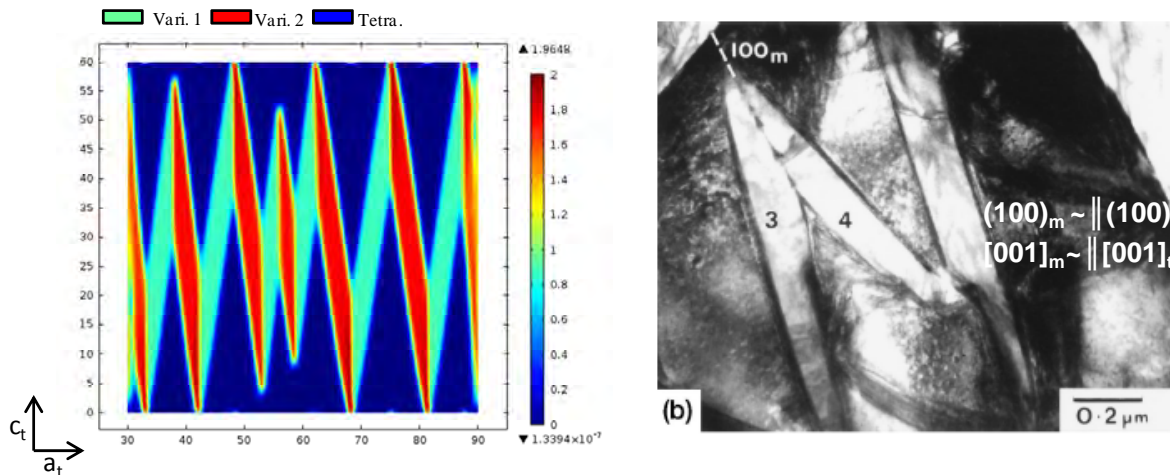
FIGURE 1. On the right, a TEM image of the monoclinic twins that formed as a result of phase transformation from tetragonal zirconia. On the left, our phase field simulation results which predict the same experimentally observed phase transition microstructure.

In addition to Model 2, Model 1 (which was partly developed in year one) was further adjusted to predict the experimental values measured for growth stresses reported in the literature. Furthermore, we completed the Micro-Raman results obtained in year one with new AFM analyses to describe in detail the transformation kinetics and morphologies that occur in the oxide scale.

The year two work led to four deliverables:

- A review of phase field modeling of the martensitic phase transformation.

- A phase field model for displacive martensitic phase transformation from tetragonal to monoclinic zirconia. As illustrated in Figure 1, the model reliably predicts the microstructure of the transformation as reported in literature.

- Identification of growth morphologies of the tetragonal phase at early stages of oxidation through combined Raman and AFM.

- A micromechanical Eshelby based model for crack patterning in oxide scale.

Benefits to DOE

Accurately predicting breakaway oxidation will ultimately help extend the service life of the current fleet of nuclear reactors, reduce down times that increase the cost of energy production, and refine designs of the next generation of nuclear reactors. The developed phase field model of phase transition and the micromechanical model of crack patterning are necessary to predict breakaway oxidation thresholds in year three. These experimentally validated models will benefit the work of those in charge of assuring safe and secure management of nuclear materials and radioactive waste under DOE's Light Water Reactor Sustainability and Consortium for Advanced Simulation of Light Water Reactors programs. A broader impact will be on the future development of experimentally validated predictive tools to characterize solid state phase transformation in various material alloys in a variety of environments.

Relevant Publications and Presentations

Asle Z., H. El Kadiri, M. Khafizov, and Z. Utegulov, "Effects of Internal Stresses and Intermediate Phases on the Coarsening of Coherent Precipitates: A Phase-Field Study," *Current Applied Physics,* Vol. 12, 570-580, 2012.

Mamivand, M., A. Zaeem, and H. El Kadiri, "A Review on Phase Field Modeling of Martensitic Phase Transformation," *Computational Materials Science,* 2012. (submitted)

El Kadiri, H., Z. Utegulov, and M. Khafizov, "Transformation and Cracks in Zirconia Films Leading to Breakaway Oxidation of Zircaloy," *Acta Materialia,* September 2012. (submitted)

Asle, Z. and H. El Kadiri, "Experimental and Phase-Field Studies of Oxidation Mechanisms of Zirconium Alloys," *Acta Materialia,* 2012. (in preparation)

"Phase Field Simulation and Experimental Studies of Zirconium Oxidation," *TMS 2012, Orlando FL, March 11-15, 2012*.

Characterization of Nanomechanical Response of Material to Determine Key Variables in Stress Corrosion Cracking

John Jackson, William Gerberich,[1] and Andre Mkhoyan[1]
11-043

Although stress corrosion cracking (SCC) has been a known issue for many decades, the mechanisms responsible for stress corrosion crack initiation and growth are complex and not well understood. The goal of this project is to investigate the primary factors contributing to SCC in reactor systems through the use of nanomechanical testing. Much of the background data on cold work, fatigue, creep, and SCC of austenitic alloys suggests that near surface nucleation of dislocations is critical to the initiation of damage leading to SCC. We are studying the use of nano-pillars fabricated using a focused ion beam to provide a test bed for chemo-mechanical mapping of crack initiation and propagation mechanisms. This project is a proof-of-principle study using alloy 304 stainless steel and iron-nickel (Fe-Ni) thin films to demonstrate the sensitivity of material response in nano-pillar deformation experiments to the measurement of fundamental parameters that may affect stress corrosion cracking. For example, in one set of studies, the effect of surface oxidation on dislocation velocities can be measured. Ultimately, through the use of this type of testing, we hope to reduce the number of experimental time-steps required to reach a conclusion about which mechanistic phenomena are most logical to pursue in detail to provide a better mechanistic understanding of SCC. Understanding of the mechanistic basis by which SCC occurs may lead to development of SCC resistant replacement materials for light water reactors or better SCC mitigation processes.

Summary

Refinement of the ion milling technique used to produce nano-pillars consumed a large part of the first year of this project. This work included milling an analog material (silicon) to refine system parameters, followed by the milling of 304 stainless steel pillars. A tribo-indenter was used to obtain baseline material properties for the 304 stainless steel nano-pillars and to determine the correct aspect ratio and geometry for the nano-pillars that gives optimally consistent data. A material of interest to the nuclear industry (Nitronic 50) was obtained and cold worked to nominally 20% (0.2 in./in. ductile strain). The cold work is known to increase the material susceptibility to SCC. This material will be used to study the fundamental differences between materials that lead to SCC. Efforts during the first year also resulted in production of thin films for transmission electron microscopy studies to determine grain boundary characteristics of the 304 stainless steel and the cold worked Nitronic 50.

The second year of effort for this project produced stress-strain data for nano-pillars of multiple sizes ranging from 300–1600 nm. A size effect exhibited by the nano-pillars of Nitronic 50 material was noted as the yield strength increased with decreasing size. Additionally, load drops that were attributed to either grain misorientation or twin boundary stoppage in larger volumes were noted to increase in magnitude as pillar size decreased. Grain boundary triple points were identified as optimal locations for ensuing studies on hydrogen charging due to enhanced plasticity.

Year two of this study also included development of an improved method for manufacturing nano-pillars via a ladder-base method with multiple sub-millings method. Additionally, a protective platinum cap was employed to improve the loaded surface of the nano-pillars. These two improvements served to improve aspect ratio for the pillars (thereby improving accuracy of stress and strain calculations) and improve contact of the nano-indenter with the top of the pillars. Following these improvements in nano-pillar production, two methods were tested for hydrogen charging. First an electrochemical process was attempted; this process was deemed unacceptable due to development of a thick oxide film that completely occluded the nano-pillar. The second method utilized gas phase hydrogen flowing over the pillar under high temperatures. This method proved successful in charging the Nitronic 50 pillars and mechanical properties were subsequently measured as a function of hydrogen charging. It was found that hydrogen charging of 1,600 nm diameter nano-pillars resulted in an approximate doubling of yield strength. Additionally, formation of a brittle surface layer on the pillars was noted; examination of this surface layer is ongoing.

[1] University of Minnesota

Benefits to DOE

Work on fundamental issues in crack growth has recently been funded by DOE's Office of Science, and further interest is anticipated. The need for a quantitative predictive SCC model is well understood by the nuclear community and by the wider materials community. If successful, this project directly addresses this need and will contribute to the fundamental understanding of material failure in operating nuclear reactors. This will allow decisions to be made on re-licensing of the current nuclear reactor fleet as well as planning for future nuclear reactor design.

Relevant Publications and Presentations

Gerberich, W.W. and D.D. Stauffer, "Damage Mechanisms, Historical," *Gaseous Hydrogen Embrittlement of High Performance Materials,* an encyclopedic volume, Woodhead Publishing, U.K. Cambridge. (in press)

Gerberich, W.W., D.D. Stauffer, A.R. Beaber, and N.I. Tymiak, "The Brittleness Transition Due to Scale," *Journal of Materials Research,* Vol. 27, 552-561, 2012.

Gerberich, W.W. and E. Hintsala, "Hydrogen's Ubiquity: Fixating, Facilitating, Fracturing, Flip-Flopping," *2012 International Hydrogen Conference, Jackson Hole, Wyoming, September 9-12, 2012.*

Uncertainty Quantification of Safety Codes Using a Bayesian Approach with Data from Separate- and Integral-Effects Tests

Robert Youngblood, Jacopo Buongiorno,[1] and Joseph Yurko[1]
12-007

Large-scale "system" codes for simulating facility safety performance may contain parameters whose values are relatively uncertain—limiting confidence in the results of the simulation. In order to use the results of these simulation codes with confidence, it is important to learn as much as we can about the appropriate values of these parameters. New information from tests or operating experience is incorporated into safety codes by a process known as "calibration," which reduces uncertainty in the output of the safety code, and thereby improves its support for decision-making.

Modern analysis capabilities potentiate very significant improvements on classical ways of doing calibration, and this project is to accomplish some of those improvements. The key innovations will come from: (1) the application of an automated quantitative phenomena identification and ranking table (QPIRT) algorithm to identify dominant processes and input parameters for reactor systems codes, (2) development of safety code surrogate (code emulator) model construction algorithms, and (3) the development of an automated algorithm to assemble test data to estimate the parameter covariance matrix and accompanying inference engine for parameter calibration.

A surrogate is needed in the first place because the multivariate nature of the problem (the need to adjust multiple uncertain parameters at once to fit multiple pieces of new information) makes calibration very computation-intensive in principle. Some investigators foresee a time when supercomputing will solve this problem, but we aren't there yet. Currently, use of a fast surrogate makes certain calibration processes feasible that otherwise would not be (simulated annealing, Gibbs sampling), and additionally may make it much easier to use gradient information in the calibration process.

Summary

Work in the first year has focused on Item 2 above: how best to construct the safety code surrogate. Construction of surrogates has been demonstrated for many years now, but usually for prediction of single-variable outcomes (such as a peak value of temperature within a time history), not typically for entire time histories at once. Moreover, most traditional surrogates do not provide uncertainty information along with their predictions, but the Gaussian-

process-based code surrogates do. This will improve the soundness of the code calibration process. At this point, Mr. Yurko has demonstrated the capability to develop Gaussian-process-based code surrogates for entire time histories, and is conversant with fairly leading-edge Gaussian-process technology, including "warping" (building the Gaussian process model on a transformation of the original data, which allows the Gaussian process model to do a better job in some cases) and function factorization (constructing a complicated surrogate as a product of factors that are each built on a subspace of the whole problem).

Mr. Yurko's thesis work will focus on improving techniques for "model selection": deciding mathematically whether the current surrogate is good enough for present purposes in light of the new data or needs to be improved, including whether the underlying safety code model is adequately reconcilable with the data. In the near term, effort will focus on the case study examples planned in the original proposal: (1) feed-and-bleed in light-water reactors; and (2) inherent safety demonstrations in a liquid-sodium-cooled reactor.

Benefits to DOE

DOE's Nuclear Energy mission relies on using large-scale, system-level simulations to support decision-making for both safety and operational purposes. For example, deployment of new reactor technologies (such as small modular reactors) will need new simulation capability, and some issues in sustainability of existing light water reactors call for improved simulation as well. This project will lead to a significant improvement in the state-of-the-art of calibrating these simulations so that they better predict reality. The techniques will benefit any technology making use of system-scale simulations in its decision-making, such as National Aeronautic and Space Administration.

Relevant Publications and Presentations

Yurko, J.P. and J. Buongiorno, "Quantitative Phenomena Identification and Ranking Table (QPIRT) for Bayesian Uncertainty Quantification," *Proceedings of ICAPP 2012, Chicago, IL, June 24-28, 2012.*

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[1] Massachusetts Institute of Technology

Protectiveness and Stability of the Zirconium Oxide in Early-Phase Corrosion of Zirconium Alloys: Predictive Relations to Surface Structure and Composition

Xianming Bai and Bilge Yildiz[1]

12-026

The water corrosion zirconium (Zr) alloys cladding materials can lead to cladding failure. A fundamental understanding of the dependence of corrosion kinetics on the clad surface structure and chemistry is needed to selectively design material surfaces of better corrosion resistance. This project aims to better understand these problems in Zr and Zr-alloy corrosion at the atomic level, taking an integrated state-of-the-art surface-sensitive experimental and computational approach. We are focusing on two controlling parameters that govern the protectiveness and stability of the passive Zr oxide (ZrO_2) layer: alloying elements and microstructure (grain boundary density) of the Zr surface.

Summary

FY 2012 was the first year of this collaborative effort between INL and Massachusetts Institute of Technology (MIT). Experimentally, we studied the early-stage oxidation mechanism of Zr alloys by applying state-of-the-art surface analytical techniques. The first step was investigation into the microstructure effect on corrosion. The control of grain size and density of grain boundaries (GBs) has been achieved by thermal annealing. Figures 1a and 1b show the microstructure of Zr samples before and after grain coarsening. Specimens were introduced into an ultra-high vacuum system (base pressure $<2*10^{-9}$mbar), heated to 373°K, and exposed to controlled oxygen environment ($2*10^{-6}$mbar). Figure 1c shows the Zr 3d x-ray photoelectron spectroscopy spectrum at t = 0 min, 5 min and 10 min of oxidation. Two peaks appear at 183.4eV and 185.8eV. These peaks indicate formation of the oxide. As oxidation proceeds, the oxide contribution becomes more evident in the spectra. Remarkably, after the same time of exposure (5 min), more oxide formed on the small-grained sample surface (Figure 1d). These results suggest that the initial surface oxidation process is controlled by the diffusion or incorporation of oxygen along the GBs of the Zr substrate, consistent with literature reports of initial oxidation. This is also consistent with the argument that the film growth with respect to time is approximately followed by a cubic kinetics rather than a parabolic kinetics. The rate-limiting step should be the transport of oxygen or electron through the initial oxide layer, which is controlled by diffusion along GBs rather than bulk diffusion in cubic growth kinetics. Scanning tunneling microscope/spectroscopy studies are ongoing on these samples.

Parallel to our experimental efforts, our computational work began by investigating oxygen transport mechanisms in the tetragonal ZrO_2. The anisotropic diffusion mechanisms of anions and cations were investigated with molecular dynamics and temperature accelerated dynamics simulations. We found that oxygen interstitials have strong anisotropic diffusion (Figure 1e), while oxygen vacancies have isotropic diffusion. The Zr interstitials have 1-D diffusion at low temperatures but 3-D diffusion at high temperatures. We studied the effects of strain (induced by oxide growth) on oxygen migration barriers. We found that the compressive strain increases the migration barriers, while the tensile strain decreases the migration barriers at small strains but increases the barriers at large strains for both oxygen interstitials and vacancies (Figure 1f). This trend agrees with experimental studies of oxygen vacancy diffusion in cubic ZrO_2 in the literature. We started the investigation of oxygen transport along GBs in tetragonal ZrO_2. Preliminary results show that the oxygen diffusion at GBs strongly depends on the grain boundary structure. At some GBs, oxygen defects are trapped so that the oxygen transport at GBs is much slower than in bulk (Figure 1g). At some other GBs, oxygen defects can diffuse perpendicularly across GBs, which is equivalent to GBs not existing. These results suggest that GBs in tetragonal ZrO_2 may not serve as fast transport paths for oxygen transport, contradictory to conventional wisdom. Additionally, we performed Ab initio-based density functional theory calculations in order to explain the effect of Nb on oxygen defect concentrations in tetragonal ZrO_2. We also investigated the stability of different defect configurations under oxygen-rich and oxygen-poor conditions. A preliminary Kröger-Vink diagram was developed for both native defects and Nb-related defects. The outcome will be compared with our previously calculated Kröger-Vink diagram for pure tetragonal ZrO_2 in order to elucidate the impact of Nb.

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[1] Massachusetts Institute of Technology
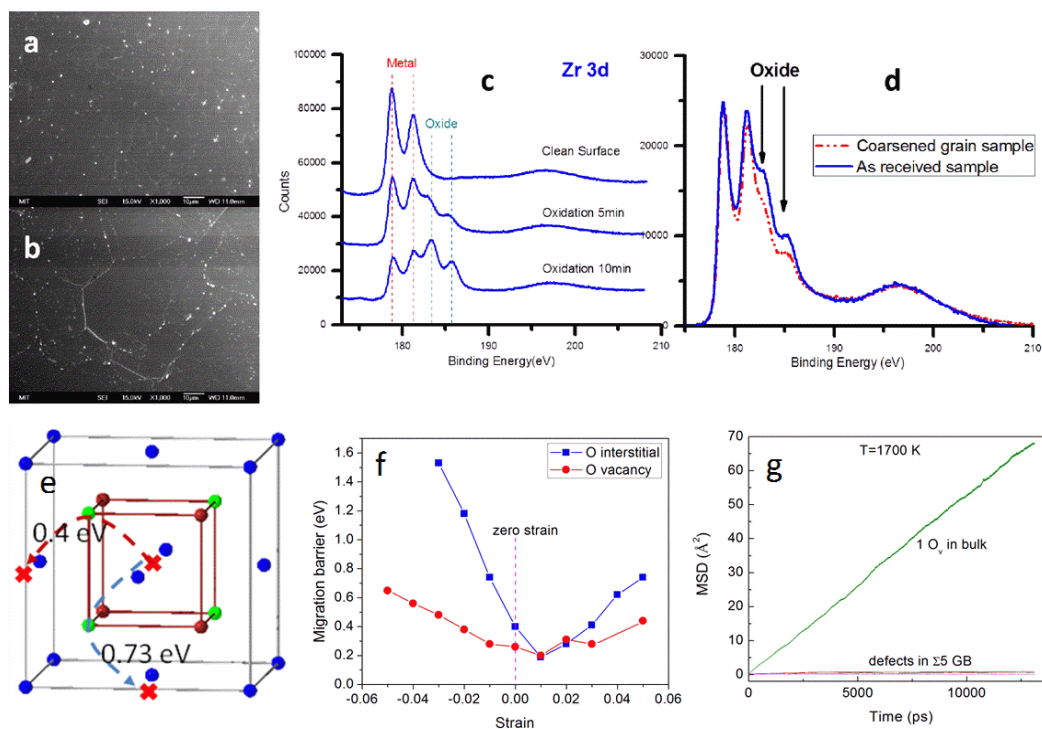
FIGURE 1. Experimental and theoretical results of oxidation in Zr: (a) as received sample, grain size ranged from 3-10 μm; (b) sample after annealing, grain size ranged from 10–30 μm; (c) Zr 3-D spectrum at different oxidation times; (d) comparison of the oxidation on different samples after 5 min oxidation; (e) anisotropic diffusion mechanisms of oxygen interstitials in ZrO_2; (f) train effects on oxygen defect migration; and (g) oxygen defect diffusion in bulk and at Σ5 (210) tilt GB.

Benefits to DOE

This work could help guide the design of corrosion-resistant Zr alloys for cladding and improve nuclear energy safety and economics while reducing the carbon footprint of the energy sector. Our work will contribute to DOE's leading role on basic science research of materials behavior and performance in extreme environments. The investigation of materials in extreme environments is a strategic growth and collaboration interest area for both INL and MIT.

Relevant Publications and Presentations

Bai, X.M., "Computational Studies of Oxygen and Zirconium Diffusion in Tetragonal ZrO_2 Related to Zirconium Corrosion," *2012 Computer Simulations of Radiation Effects in Solids (COSIRES 2012), Santa Fe, NM, June 2012*.

187

Science-Based Simulation Model of Human Performance for Human Reliability Analysis

Ronald Boring, Carol Smidts,[1] and Ali Mosleh[2]
12-043

To date, much of human reliability analysis (HRA) has been developed as a series of methods to address requirements of probabilistic risk assessment (PRA). This PRA emphasis has resulted in a piecemeal collection of methods and practices that in many cases lack a scrutable scientific underpinning. This approach has also left HRA ill prepared to address current issues such as beyond-design-basis accidents. This project addresses this shortcoming by improving two fundamental areas of HRA: (1) the data basis, by developing an approach to collect human performance data at the Ohio State University (OSU) and INL control room simulator facilities; and (2) the ability to model dynamic phenomena by expanding the Information-Decision-Action-Crew (IDAC) dynamic simulation engine at the University of Maryland (UMD).

Dynamic HRA has been an area of considerable interest to newcomers to HRA like aerospace and the oil industry, which have multiple phases of operation and have found little utility in static, single-phase models. The proof-of-concept of tying a dynamic HRA simulation engine with empirical data sources in this project sets the stage for other industries that are waiting for clear demonstrations before investing in HRA.

Currently, HRA (and to a large extent related PRA) activities at INL are focused on traditional static models. Static PRA and HRA models are the mainstay of current risk and reliability programmatic work, but already the long-term utility of such approaches is being called into question. These static models capture only a snapshot of plant and operator performance, but the models cannot readily be adapted to respond to complex event evolutions, including those that might be found in severe accidents. The need to model events dynamically and to understand the human impact on the successful resolution or tragic escalation of events is crucial to the future of risk and reliability.

Summary

A prerequisite for empirical human performance data collection and dynamic simulation is a realistic control room scenario. Nuclear power plants are operated from main control rooms. In order to train operators for proper decision making and action at the plant, every plant in the

U.S. is required to have a control room simulator. Scenarios are developed by researchers and trainers to ensure operators have a broad exposure to different plant upset conditions. These conditions occur rarely; thus, training ensures operators are adequately prepared to respond to such conditions. INL reviewed abnormal operating scenarios for potential use in INL's and OSU's simulators and for modeling in UMD's IDAC. A set of factors was reviewed for guiding the selection, including the applicability across different reactor types and designs, speed of the accident progression, potential for operator misdiagnosis, the mix of cognitive and physical responses, and availability of emergency operating procedures (EOPs). This process resulted in the selection of a small loss-of-coolant accident (LOCA) simulation as the initiator. The research team began planning a small LOCA scenario for implementation in FY 2013.

Leveraging previous efforts, both INL and OSU completed significant work on deploying their respective control room simulators for research applications. In order to have a common platform for research, both INL and OSU have purchased licenses to GSE's generic Pressurized Water Reactor (gPWR), which has recently been installed at both locations.

For the present project, the research team developed the data collection tools used in control room simulator studies. In conjunction with INL, OSU optimized its control room layout with respect to human factors concerns and for data collection. The research team jointly reviewed and acquired necessary recording equipment to allow data collection during the operator-in-the-loop studies planned in FY 2013. OSU performed a literature and technical review of performance shaping factors (PSFs) commonly used in HRA methods and established a list of PSFs that can be evaluated successfully in control room simulator studies. These PSFs will serve as the basis for data collection to support and validate HRA methods.

The IDAC model is an important component of this research as it provides a tool that can dynamically predict operator performance in changing situations. The UMD team completed its evaluation of the optimum path for integrating the IDAC simulation model with the INL and OSU simulators, considering practical issues (e.g., the scale of changes in the code and level of knowledge transfer between UMD and other team members), short term needs of the project, and extent of capabilities

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[1] Ohio State University

[2] University of Maryland

needed for any future expansion of the scope. The research team determined that the optimum path would be to link the entire IDAC platform with the OSU simulator. In this context, IDAC serves as a "virtual operator" that makes decisions and acts upon simulator parameters. UMD provided a walkthrough of the IDAC architecture, features, programming environments, sample input files, and the communication protocol between IDAC operator model and RELAP5 thermalhydraulic code. To support the interaction of the IDAC virtual operator to the INL and OSU simulators, UMD developed a sample virtual operator that followed the EOPs associated with the small LOCA scenario. This virtual operator code will be further refined in FY 2013 and benchmarked against actual operator performance in the control room simulator. Once validated, the IDAC virtual operator can be used for modeling operator performance across a much wider range of situations than is possible in current static HRA models.

This foundational research in FY 2012 has provided a unique opportunity to take advantage of the interests and experience of the research team. This research has the potential to fundamentally change the way data are gathered to inform HRA. The incorporation of significant new PSF data sources as well as the potential for increased data feeds to HRA methods offers the potential to take HRA from the current use of static models with a limited empirical basis to dynamic models based on sound psychological research and with an explicit empirical foundation. By empirically validating operator performance against the human performance predictions from HRA, this research will reduce the uncertainty surrounding HRA estimates. By enhancing the understanding of operator performance in upset conditions, such research also provides the possibility of substantially enhancing the safety of plants in the longer term.

Benefits to DOE

This LDRD supports the DOE-NE Light Water Reactor Technologies program goal of "extending the operating lifetimes of current plants beyond 60 years and, where possible, making further improvements in their productivity will generate early benefits from research, development, and demonstration investments in nuclear power."

This project firmly plants INL at the forefront of dynamic HRA research and provides INL the opportunity to develop a joint testbed for validating more complex and dynamic-capable HRA models such as IDAC.

Relevant Publications and Presentations

Boring, R., D. Kelly, C. Smidts, A. Mosleh, and B. Dyre, "Microworlds, Simulators, and Simulation: Framework for a Benchmark of Human Reliability Data Sources," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, 2012*.

Gupta, A., R. Benish, M. Li, and C. Smidts, "Validating THERP: An Approach to Experimentally Validating the Human Error Prediction Rates in the THERP Tables," To be presented, *American Nuclear Society Winter Meeting, Washington, DC, November 10–15, 2013*.

Mosleh, A., S.H. Shen, D.L. Kelly, J.H. Oxstrand, and K.M. Groth, "A Model-Based Human Reliability Analysis Methodology," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference*, 2012.

Sundaramurthi, R., "Human Reliability Modeling for Next Generation System Codes," M.S. Thesis, Nuclear Engineering, Ohio State University, 2013.

Sundaramurthi, R. and C. Smidts, "Human Reliability Modeling for Next Generation System Codes," *Annals of Nuclear Energy.* (in press)

Boring, R., D. Kelly, C. Smidts, A. Mosleh, and B. Dyre, "Microworlds, Simulators, and Simulation: Framework for a Benchmark of Human Reliability Data Sources," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, Helsinki, Finland, June 25–29, 2012*.

Li, Y. and A. Mosleh, "Simulation of Nuclear Power Plant Operators Reasoning Process for Situation Assessment in ADS-IDAC Dynamic PRA Platform," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, Helsinki, Finland, June 25–29, 2012*.

Mosleh, A., "Delivering on the Promise: PRA, Real Decisions, and Real Events," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, Helsinki, Finland, June 25–29, 2012.*

Mosleh, A., S-H. Shen, D.L. Kelly, J.H. Oxstrand, and K.M. Groth, "A Model-Based Human Reliability Analysis Methodology," *Presented at Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, Helsinki, Finland, June 25–29, 2012.*

Recovery of Precious Metals from Used Nuclear Fuel and Electronic Waste Using Sulfur-Impregnated Nanoscaffolds

Peter Zalupski and Linda Nazar[1]
12-056

Ordered mesoporous carbons (OMC) are nanostructured carbon materials characterized by hexagonal, porous molecular framework. The most attractive property of such materials is their porosity of mesoscale dimensions. The diameters of typical pores of mesoporous materials range between 2 and 50 nanometers. As such, a mesoporous framework may be envisioned as the architecture constructed from nano-sized building blocks. This project is evaluating the use of mesoporous carbons in hydrometallurgical recovery of precious metals (such as platinum, gold, and palladium) from aqueous acidic waste streams.

The Special Section of the August 10, 2012 issue of Science magazine has been devoted to the challenges associated with the growing production of consumer byproducts. Entitled "Working with Waste," the series of articles highlight the importance on focusing on the recovery of valuable materials. This LDRD project cultivates the belief that our waste may indeed be called treasure instead of trash.

Summary

Mesoporous carbons are engineered agglomerates of carbon nanotubes held together by small carbon nanofibers. They exhibit a uniform pore diameter, high pore volume, and high channel permeability. Figure 1 illustrates a simplified cross-section of possible mesoporous carbons architecture, where each circle corresponds to one carbon nanotube. The depth dimension represents the length of the mesoporous structure, which commonly measures several micrometers. Such mesoporous assembly may span ~100 channels—i.e., carbon nanotubes of 6-7 nanometer diameters—interlocked into hexagonal unit cells by carbon nanofibers to create wide 3-4 nanometer channel voids. Such porous agglomerates, when coated with molecular sulfur, exhibit attractive affinity for precious metals such as platinum, gold, and palladium.
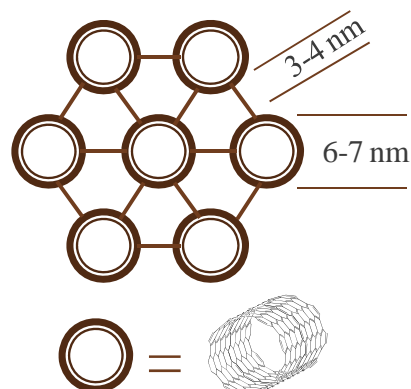
FIGURE 1. Simplified cross-sectional representation of possible mesoporus carbon architecture.

First year research accomplishments include:

- The initially tested OMC material, denoted CMK-3/S, contained 10% sulfur. The sorption capacity and kinetics of platinum uptake from mildly acidic aqueous solutions (220 mg Pt/gram of sorbent) is very competitive with commercially deployed SAMMS materials (self-assembled monolayers on mesoporous silica). Significant room for improvement is still available as sulfur content may be increased fivefold.

- Engineered forms of CMK-3/S based on polyacrylonitrile polymer support have been prepared.

- The sorption affinity of the tested sulfur-coated mesoporous carbon for palladium exceeds that of platinum.

Research in FY 2012 identified very promising precious metal uptake features of sulfur-coated mesoporous carbons. The upcoming year will focus on competitive sorption—where mixtures of metals are present—seeking preferential sorption of precious metal ions. Mesoporous carbons of different structural features (porosity and particle size for example) and different sulfur content will also be examined (Figure 2).

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[1] University of Waterloo, Canada
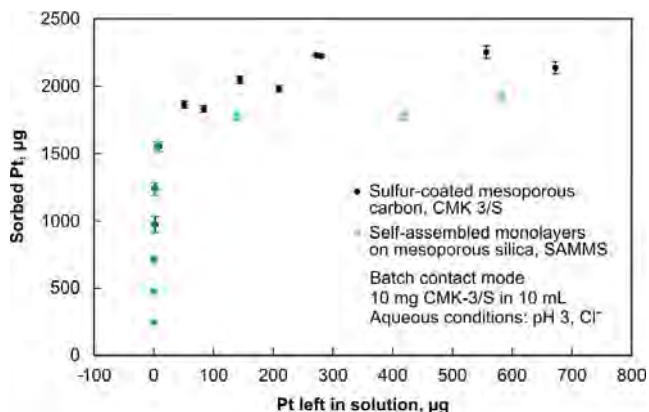
FIGURE 2. Sorption of platinum on sulfur-coated mesoporous carbons, compared with SAMMS materials.

The promising metal uptake results have been observed in aqueous media of varying concentrations of hydrochloric acid. Several studies are in progress:

- Simulant solution for electronic scrap materials containing copper, iron, aluminum and nickel

- Leaching of two types of electronic scrap materials— cell phone circuit boards and computer circuit boards—has begun as a treatability study after permissions from the State of Idaho's Department of Environmental Quality were obtained.

Benefits to DOE

Through the sponsorship of this project, DOE is participating in the growing global movement of finding efficient and beneficial uses of consumer waste byproducts. If sustained, such efforts will ease the challenges of supporting our society for years to come. In addition, precious metals are used in a variety of energy-related applications, such as catalysts in extreme environments. Currently, rare earth precious metals are considered critical components of energy systems and the global supply of such materials is a concern for all nations. This project provides a potential unique source for these critical materials.

Relevant Publications and Presentations

None.

Chemistry and Flowsheet Development for Lanthanide Separations

Scott Herbst, Peter Zalupski, and Mikael Nilsson[1]
12-059

The lanthanide series consists of the 15 elements with atomic numbers 57 through 71 (lanthanum through lutetium), all occurring naturally with the exception of promethium. The term rare earth elements (REE) is often used interchangeably with "lanthanides," but typically includes chemically similar yttrium (Y) and scandium (Sc). This convention is adopted in this report. The exceptionally similar chemical characteristics of REE are attributed to their existence in the characteristic and very stable trivalent (+3) oxidation state. This universal preference for the +3 oxidation state and the notable similarity in atomic radii (size), results in great difficulties during the chemical separation and concomitant purification of these elements. In fact, the separation and purification of the individual REE from one another, and particularly of adjacent lanthanides, is perhaps the most difficult and challenging separations problem faced by modern day separation scientists. Existing INL expertise in lanthanide chemistry and flowsheet development, coupled with resources and equipment developed for nuclear fuel cycle applications, will be leveraged to develop and test efficient solvent extraction (SX) flowsheets for the separation, purification, and concentration of the individual REE from each other. The goal is to design and test flowsheets that will significantly improve process economics by utilizing one or more of the following principles: increased throughputs, improved separation factors, reduced chemical costs/inventories, reduced waste costs, or reduced conversion costs for products.

It is noteworthy that elevated interest in REE processing and economics at the INL level (as witnessed by this LDRD), at the DOE level (with the Critical Materials Energy Innovation Hub funding opportunity announcement), and at the industrial level (Molycorp/INL Work for Others project) were not fortuitously superimposed events. Rather this set of events provides testimony of an urgent national sense to address shortfalls in REE supply.

Summary

Much of the effort during the first year of this project revolved around the development of analytical capabilities to determine REE concentrations in samples from SX experiments. Typical analyses of REE mixtures in liquid samples are based on inductively coupled plasma mass spectroscopy (ICP-MS) methods and can take weeks to complete due to the rather cumbersome and complicated series of procedures required to obtain even single element analyses from experimental samples. Multi-element analysis by the ICP-MS method is extremely sensitive and generally quite accurate, but rather time consuming and expensive; consequently, ICP-MS is reserved for only the most important proof-of-concept experiments, and is not the best choice for the vast series of scoping tests planned within this project. An initial investment was made in procuring many of the REE in the form of high purity (99+%) nitrate salts for use as feed stocks for the separation experiments. Additionally, samples of radioactive isotopes of Y, gadolinium (Gd), and holmium (Ho) were also obtained for determination of distribution ratios in a variety of SX tests. These materials provide a convenient analytical means to determine if extraction behavior of individual elements from a mixture of REE; Y, Gd, and Ho and can be analyzed simultaneously and directly from solutions containing mixtures of the three elements. The radiometric analysis method is also very accurate and sensitive, and provides quick analytical turnaround for scoping tests. Additionally, procurement, setup, and testing of a new Mettler-Toledo titration system was also completed during the first year of this project. This analytical equipment provides a rapid analytical means to evaluate REE concentrations in liquid solutions and can be used to evaluate single element concentrations of the REE by titerometric means with colorimetric detection using a phototrode. This method has also proven valuable for the rapid evaluation of REE behavior in experimental scoping studies and in a non-radiological environment. Finally, the analytical capabilities for this research were also expanded by our University of California, Irvine collaborators, who are developing neutron activation analysis methods for sample analysis.

Experimental scoping studies completed to date indicate that either di(2-ethyl hexyl) phosphoric (HDEHP) or trialkyl phosphine oxide (TRPO) are relevant extractants with the potential to improve separation of the individual REE. The choice of organic diluents for these extractant has a dramatic impact on the separation ability. In fact, improvements with HDEHP, which is a well-known REE separative agent, are possible with a simple change in the organic diluent used. Diluent choice also dramatically

[1] University of California, Irvine

impacts the separative power of TRPO. Preliminary data indicate that TRPO shows enhanced separation factors amongst the heavier REE elements, with the potential to provide improved process flowsheets and economics.

Enough preliminary data have been obtained to begin developing a process model and define a potential separations flowsheets for efficient separations. These data will be expanded during the first part of year two with plans to test a full separations flowsheet during the second year.

Finally, two students supported this project over the course of the summer. A chemical engineering graduate student from University of California, Irvine and an undergraduate Idaho State University summer intern both supported the project.

Benefits to DOE

Several of the REE are considered strategic for certain DOE clean energy technologies and Department of Defense applications. The outcomes of this LDRD project

have the potential to impact economics and supply of these "critical materials" in a favorable manner. Many REE have experienced substantial increases in "high tech" uses, and enable varying technologies ranging from super magnets to electric vehicles, lighting, and gasoline production. Over the past two decades, China's low mining and milling costs, concomitant with increasingly stringent environmental regulations in other countries, have resulted in the current situation where fully 97% of the world's production and supply of REE comes from China. To exacerbate the issue, Chinese limitations on REE export quotas have left international demand far above supply, resulting in dramatic price increases or even eliminating availability all together. Limited availability and increased international competition for the world's available supply has resulted in growing concern, to the point that several REE are now considered "strategic and critical materials" in the U.S.

Relevant Publications and Presentations

None.

Observation of Zirconium Oxidation at Atomic Level Using Nonlinear Optical Spectroscopy

Marat Khafizov, Kenan Gundogdu,[1] and Izabela Szlufarska[2]
12-077

Understanding the atomic level mechanisms underlying the initial oxidation kinetics of zirconium (Zr) metal will benefit further development of Zr alloys as a cladding material in nuclear fuels. We are working on an integrated approach that brings advanced spectroscopic techniques and state-of-the art first principle calculations together. Specifically, oxidation of fuel cladding limits the lifetime of nuclear fuel as it is a precursor for stress corrosion cracking that leads to mechanical failure.

We implemented Second Harmonic Generation (SHG) spectroscopy (a nonlinear optics technique), which provides bond-specific information about chemical and structural properties of interfaces. We use this technique to study the formation of an initial oxide layer on the surface of single crystal Zr metal and its alloys. In conjunction with the SHG experiments we perform *abinitio* calculations based on the density functional theory (DFT). These calculations are highly accurate and particularly beneficial in discovering preferential bonding of oxygen in Zr alloys as a function of applied strain. In addition, advanced, time-dependent DFT methods are used to quantify hyperpolarizabilities of Zr-O bonds. The results of those calculations are applied to interpret the SHG spectra.

Summary

An ultra high vacuum chamber with optical windows, ion milling, and an Auger spectrometer was set up and tested. An experimental protocol to prepare smooth, clean, oxide free metal surfaces has been established, and the applicability of the SHG approach to examining zirconium oxidation has been demonstrated at ambient conditions. Our major finding is that the oxidation interface gives rise to a rotationally anisotropic signal suggesting the presence of a well ordered interface with three types of bonds. Figure 1 shows a typical SHG spectrum where the three peaks correspond to three bond types at the interface. Currently, we are fitting the theoretical data obtained by DFT calculations to the anisotropic SHG signal. The result will be used to establish a direct correlation between the interface bonds and the experiment.
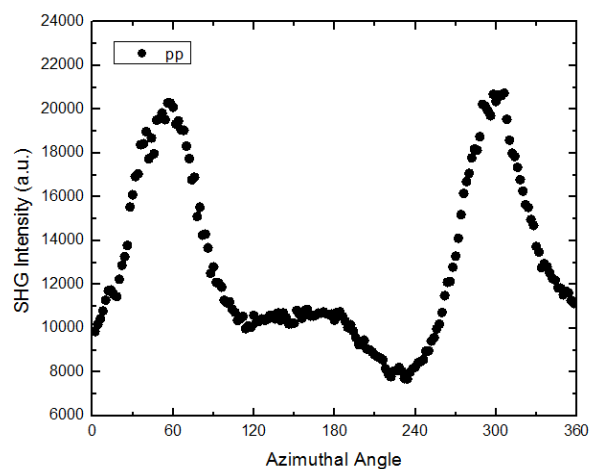
FIGURE 1. Rotationally anisotropic second harmonic spectrum of a freshly oxidized Zr (0001) sample.

The modeling part of the project has been focused on investigating the effect of strain on oxygen incorporation into Zr. Strain in Zr can be introduced by the lattice mismatch between Zr and the growing oxide or by stresses exerted on the cladding during operating conditions. Here, calculations based on the DFT were performed to investigate adsorption of oxygen on a Zr (0001) surface. Both tensile and compressive strains have been considered, and oxygen coverage was varied from 0.11–1.00 monolayers. We demonstrated that adsorption of oxygen into the first few layers of Zr is affected by surface strain and interactions between adsorbed oxygen atoms. Oxygen binding energy was found to increase as the strain changes from tension to compression (Figure 2). When oxygen coverage is low and the interaction between adsorbates can be neglected, surface face centered cubic sites (SFCC) are found to be the most favorable binding sites. However, increasing coverage and/or exerting a compressive strain stabilizes octahedral sites between the second and third Zr layers (Octa23). This shift is due to the fact that, under the aforementioned conditions, repulsive force between adsorbates is lower in the bulk where electrostatic interaction is screened. Our results demonstrate that compressive strain at the Zr-oxide interface will drive oxygen from the surface into the bulk of the material.

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[1] North Carolina State University

[2] University of Wisconsin
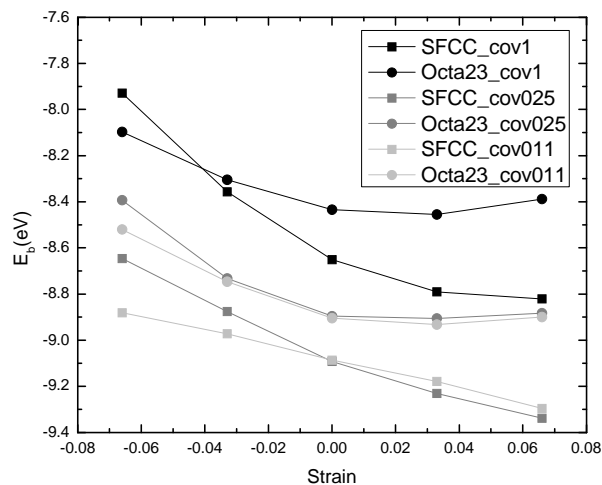
FIGURE 2. Oxygen binding energy of two different binding sites on a Zr (0001) surface under different strain and coverage conditions. (SFCC: surface face center cubic sites; Octa23: octahedral sites between 2nd and 3rd Zr layers.) Negative and positive strain values correspond to tensile and compressive strains, respectively.

We also calculated oxygen binding energy with the multiple layer absorption model and found it gives a lower binding energy than a single layer adsorption model at high oxygen coverage. These results are now being prepared for publication. Future studies will include calculations of the structure and energetics of a zirconium oxide-zirconium interface. These calculations will support experimental efforts in this project and provide a basis for modeling nucleation of oxide in Zr metal.

Benefits to DOE

The results of this work will help further understanding of a corrosion mechanism of nuclear fuel at the fundamental level, benefitting the Advanced Light Water Reactor Fuels R&D pathway of the Light Water Reactor Sustainability Program. The results also provide important experimental data for the modeling efforts of the Consortium for Advanced Simulation of Light Water Reactors. This work establishes an additional experimental capability for performing studies of corrosion interfaces, and it could further be expanded to interfacial chemistry studies relevant to the Fuel Cycle Research and Development Program.

Relevant Publications and Presentations

The results of this project are scheduled to be presented at the 2012 MRS Fall Meeting and the TMS 2013 Annual Meeting. Manuscripts for peer reviewed journals are in preparation.

Development of Emissivity-Tuned, Robust Encapsulated Radioisotope Heat Sources for NASA's New Advanced Radioisotope Thermo-Photovoltaic Power System

Carl Stoots, Robert O'Brien,[1] and Troy Howe[1]
12-090

Current National Aeronautics and Space Administration (NASA) space power systems use the General Purpose Heat Source containing a radioisotope thermal inventory of about 250 W coupled to either a thermoelectric or Stirling engine-based conversion process. Thermoelectric-based conversion cycles suffer from low conversion efficiency while Stirling engines have moving parts, leading to concerns of long term reliability. This research program is investigating the coupling of novel radioisotope heat sources for electrical power generation through thermo photovoltaic (TPV) conversion to produce a system design with a target specific mass of 40 to 80 kg/kWe. A system with such power performance would be up to a factor of 9 times greater than the current state of the art while eliminating moving parts. Radioisotope encapsulation processes are being developed using nuclear material surrogates via the Spark Plasma Sintering (SPS) process and surface emission spectrum tuning will be developed via modification of surface features, laser additive manufacturing, dopants, and other methods. These processes will be developed to investigate the feasibility of producing compact, high temperature heat sources that have suitable mechanical strength to endure conceivable launch accident scenarios while optimizing the surface emissions performance for optical coupling with thermo photovoltaic converters. Integral concept feasibility will be tested using a custom-built INL test facility.

Most of the INL research investigated the new radioisotope encapsulant. This novel encapsulated radioisotope heat source is based on a tungsten-rhenium cermet matrix for use in conjunction with NASA's InGaAs TPV cells. Other cermet matrices, including W-Ta and Ti-Ta, will be evaluated as potential reduced-mass candidates for isotopic encapsulation. Here the emissivity and luminescence spectrum of the surface will be optimized for the band gap of the TPV cells (~0.6 eV or 2,000 nm) while the structure of the heat source matrix will be developed to provide robust and stable containment during operation at high temperatures and in accident conditions. More specifically: (1) Production of prototypic radioisotope heat source encapsulation matrices based on a tungsten-rhenium alloy, (2) Development and characterization (surface emissivity and temperature dependent luminescence spectra) of prototypic heat source emitter/outer surfaces that have been spectral tuned via a combination of SPS and/or other manufacturing technologies, (3) Mechanical testing of various prototypic heat source matrices, including simulated ablation rates for atmospheric re-entry as well as thermal expansion and thermal conductivity, and (4) Integrated test of heated surrogate Radioisotope Thermo Photovoltaic (RTPV) heat source and PV cell conversion system within a thermal vacuum chamber.

Summary

Progress in the first year of this LDRD project included encapsulant samples that have been fabricated using SPS from W and W-Rh with and without ceramic fuel surrogates. Heat transfer calculations have been performed for an emission spectrum measurement facility. These model results (CFD analyses) were used to specify and order a thermal vacuum chamber. This chamber has been received and is installed. Calculations also showed that the initial concept of using a 10 W continuous output laser would not be sufficient to heat samples to the desired temperature range when estimates for apparatus heat losses are accounted for. A larger (100 W continuous) laser was purchased and has been delivered. Improved means of insulating the target encapsulants within the thermal vacuum chamber have been devised and are being fabricated using analysis results. Heat transfer analyses have been started for a coupled encapsulant – PV system within the vacuum chamber, looking at heating requirements and heat losses. Based upon these analyses, a conceptual prototype system has been designed and modeled using the COMSOL Multiphysics code. (Assembly of the experiment/test facility is underway.)

Personnel negotiated the use of the NASA Atmospheric Arc Jet facility for testing of RTPV components and subsystems under the simulated conditions of atmospheric reentry. It is likely that sample/surrogate encapsulants will be sent there for testing in FY 2013.

Benefits to DOE

The currently limited availability of ^{238}Pu for space nuclear power systems has prompted NASA to investigate novel and alternative power conversion mechanisms whose use over current thermoelectric and Stirling power conversion technologies would yield both higher power conversion efficiencies and an overall reduction in the system specific mass (kg/kW$_e$) of radioisotope power systems. New technologies such as this project's concept would:

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[1] Center for Space Nuclear Resource

(1) alleviate the pressure on existing ^{238}Pu supplies,
(2) enable longer and more reliable mission designs, and
(3) enable the development of compact spacecraft based upon the Cubesat chassis (of interest to Department of Defense and National Nuclear Security for satellite applications and NASA deep space flight).

Relevant Publications and Presentations

Howe, T., R.R. O'Brien, and C. Stoots, "Development of a Small-Scale Radioisotope Thermo-Photovoltaic Power Source," Nuclear and Emerging Technologies for Space 2012, Paper 3059, Full paper, Houston, Texas, March 2012.

Stoots, C., T. Howe, and R.R. O'Brien, "Development of Emissivity-Tuned, Robust Encapsulated Radioisotope Heat Sources for NASA's New Advanced Radioisotope Thermo-Photovoltaic (RTPV) Power System," *INEST Space Power CORE Regional Outreach Meeting, Ohio State University, Columbus, OH, February 2012*.

Model Development for Transient Performance Analysis of a Small Modular Reactor in a Hybrid Energy System

Shannon Bragg-Sitton and Michael Doster[1]
12-124

Nuclear Hybrid Energy Systems (NHES) could be a key part of the solution to achieving energy security, may provide reliable power availability even with increasing renewable energy penetration into the power grid, and may allow repurposing excess electricity in times of low demand. Incorporating a fission-based power source in a multi-output system (electricity and process heat) can offer significant advantages over carbon-based production sources, such as coal or natural gas, including reduction in atmospheric carbon emissions. In an integrated multi-output system, thermal energy from the nuclear reactor subsystem can be diverted to industrial applications in times of low electricity demand. High temperature, high quality heat from advanced reactor designs might be used for hydrogen production or synthetic fuel production (coal-to-liquid or natural gas-to-liquid processes). Low temperature heat from advanced reactor designs or the current and future fleet of light water reactors (LWRs) might be applied to desalination processes or be stored for later use in low temperature ammonia or hydrocarbon-based thermal cycles.

The INL NHES research team is currently developing a dynamic simulation of an integrated hybrid energy system. A detailed simulation of proposed NHES architectures will allow initial computational demonstration of a tightly coupled NHES to identify key reactor subsystem requirements, identify candidate reactor technologies for a hybrid system, and identify key challenges to operation of the coupled system. This work provides a baseline for later coupling of design-specific reactor models through industry collaboration. The modeling capability addressed in this project focuses on the reactor subsystem simulation.

Preliminary hybrid energy system models developed by INL researchers have focused on the non-nuclear components and subsystems that comprise an NHES. The current project supports initial efforts to integrate a Fortran-based simulation of a small modular reactor (SMR) with the INL balance of plant model. This initial effort takes advantage of an existing SMR model developed at North Carolina State University (NCSU) to provide initial integrated system simulation for a relatively low cost and over a relatively short period of time. The goals of the 6-month project include:

1. Modification of the NCSU dynamic reactor simulation to represent a generic SMR concept

2. Integration of the reactor subsystem simulation with the INL-developed hybrid energy system model to allow architecture design and feasibility analysis to be conducted in future work.

Once the full system simulation has been integrated and validated, INL researchers will have the necessary tool set to assess potential NHES architectures; to define potential candidate reactor technologies for hybrid systems, with a focus on the associated operating parameters and performance; and to identify key challenges or technology gaps in implementing a nuclear hybrid energy system.

Summary

Many computational tools and methods are available for modeling a nuclear reactor, power conversion systems, and associated process applications. One method is to develop a single program capable of modeling the entire system. Another is to combine two or more existing computer programs, each modeling a portion of the system for which it is validated, where the programs exchange information to compute the solution. The former method requires a lengthy development and verification and validation process. The latter method leverages established software packages to reduce development and funding requirements.

NCSU has demonstrated experience in developing high fidelity, full plant simulators for predicting the dynamic response of pressurized water reactors during normal and off-normal operational conditions. A high fidelity model incorporating a reactor, power conversion system, and local electrical grid with sufficient detail for controls engineering developed at NCSU for preliminary investigation of SMRs as a dynamic stability aid in small electrical grid applications was identified for incorporation with the INL NHES simulation to speed the development of a full system simulation.

In preliminary NCSU investigations of the impact of SMRs on grid stability, the dynamics of the reactor primary loop were modeled by employing a simulation of the International Reactor Innovative and Secure reactor, a 335 MWe plant that features an integral primary system

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[1] North Carolina State University

design similar to several other LWRs under development. The code is written such that it can accommodate any nodalization that represents an integrated pressurized water reactor (IPWR). The Fortran-based NCSU simulation includes reactor, power conversion system, and local electrical grid modules. In the current implementation, the existing IRIS model was downsized to represent a generic 500 MWt/158 MWe IPWR with operating characteristics of interest to Hybrid Energy Systems. Relatively simple modifications to the model details allow simulation of several of the candidate light water cooled SMR designs or to assess optimal reactor design, system configuration, control system design, etc. Possible code modifications to perform these studies include component scaling, fuel pin/bundle design, reactivity parameters, pump and valve characteristics, or control system logic.

The IPWR simulator includes a model of the pressurizer, reactor core including a six delayed neutron group kinetics model, a decay heat model and a hot channel/departure from nucleate boiling model, a model of the primary flow loop, and a model of the secondary side including the steam generators and balance of plant. The simulator is capable of describing either forced flow, or natural circulation systems such as that included in the NuScale power module design. In the current IPWR simulator, a helical coil steam generator is assumed, where the secondary fluid flows on the tube side of the heat exchanger. Detailed models have been developed to describe the dynamics of steam generators of this design. Modifications to allow for more traditional Once Through Steam Generator designs, such as those incorporated in the Babcock and Wilcox mPower reactor, can be easily implemented. The stand alone reactor simulation also includes balance of plant, instrumentation and control systems, and plant protection systems including the normal spectrum of reactor trips and engineered safety features. Options are available to degrade sensor signals for flow, level, pressure, etc. as the result of noise and drift, in addition to failing the sensor all together. Additional sensor models can be easily added. The simulator models also provide ease of access to correlations for heat transfer, pressure loss, void fraction, etc.

The full NHES simulation requires dynamic coupling of the reactor subsystem simulation with the remaining hybrid system components. The INL-developed balance of plant simulation includes power conversion, renewable energy

(wind in the current implementation), energy storage grid integration, and a process application that utilizes reactor-produced thermal energy. Hence, only some components from the NCSU SMR model are being incorporated with the integrated NHES simulation. The coupling of the NCSU and INL simulations is accomplished at the interface between the primary and secondary sides of the steam generator. Hence, the balance of plant components of the SMR simulation (everything downstream of the steam generator) provides boundary conditions for model validation prior to integration of the full NHES simulation. Details of the reactor simulation validation process are provided in INL/EXT-12-27357.

The non-reactor component and subsystem models are written in the Modelica language, utilizing the Dymola software package to translate the various component descriptions into a set of solvable equations; the full balance of plant simulation is then coupled to powerful mathematical solvers in MatLab. A co-simulation approach is necessary to integrate the reactor simulation with the remainder of the hybrid energy system simulation; several possible approaches to this integration were investigated.

Reactor Subsystem Description. The SMR subsystem model includes models for the reactor vessel, reactor core/neutronics, components, sensors, and valves. The reactor vessel model is highly detailed, including coolant downcomers, a steam generator region, lower and upper plena, the core region (described by four axial nodes), risers, pump inlet plenum, and pressurizer. The vessel dimensions are scaled to fit a candidate SMR design, but can be modified given design detail from other vendors. Individual component models allow further definition of the pressurizer, pumps (for forced convection designs) and steam generator in the system. The once-through helical coil steam generator model (which can be toggled to a straight tube design by changing heat transfer coefficients and friction factors) includes details such as the number of tubes, tube length, diameter, pitch, and tube thermal conductivity. Pump models are tied to actual pump curves and are designed such that a pump trip can be simulated.

Multiple calculations are performed in the reactor core/neutronics module. This module returns neutron power, decay heat power, peaking factors, fuel pin surface heat transfer rates, and energy deposition in the coolant. Reactor kinetics are based on the 6-group point kinetics equations, with explicit definition of moderator and fuel

feedback and Xe and Sm production. The current version assumes a 17 × 17 fuel bundle for heat transfer and pressure drop calculations and performs both average and hot channel calculations, returning average and peak fuel rod temperature. Either forced or natural convection cooling can be simulated.

Additional files are referenced by the program to simulate instrumentation input (sensors file) and realistic components (valves file). The sensors file provides sensor input to the control system model and can simulate sensor drift and noise, such that the impact of degraded performance on the control system can be analyzed. The valve characteristics file defines flow area through a specific valve, loss coefficients versus valve position, valve time constants, dead time and hysteresis.

Model Integration. The full simulation of a nuclear hybrid energy system requires dynamic coupling of the reactor subsystem simulation with the remaining hybrid system components. The reactor subsystem includes both the basic models and the solution of those models; this is referred to as a *simulation* rather than a *model*. Hence, a co-simulation approach is necessary to integrate the reactor simulation with the remainder of the hybrid energy system simulation. Several possible approaches to this integration were investigated.

Developed by Lawrence Berkeley National Laboratory, the Building Controls Virtual Test Bed (BCVTB) is a modular, extensible, and open-source platform software environment that is designed to facilitate co-simulation between a diverse set of programs. BCVTB uses a Java-based graphical user interface to visually build the high-level system and connects the different programs, allowing them to exchange data through the time integration.

The Fortran simulation has been adapted to the BCVTB format, recompiled, and run within that software environment. Prior to establishing linkages between the

reactor and balance of plant simulations the individual components were shown to be independently functional within the BCVTB environment. The BCVTB software was easily linked to the Matlab/Simulink and Modelica environments, with the primary challenge being to link the Fortran simulation to the other components within the BCVTB framework, facilitating data exchange.

Linking to the routines referenced by the interfaces in Fortran proved to be challenging. A very simple set of independent simulations were created in each environment (i.e., Fortran and Modelica) to allow the developers to become familiar with linking simulations in the BCVTB prior to attempting the more complex simulations. The various program versions used to accomplish a fully linked simulation include Java JDK version JDK6u35, Intel Fortran Compiler 11.1.072 and Visual Studio 2010 Professional. Several trial simulations were run using different Fortran source files. Accomplishing a co-simulation with the more complex hybrid energy system components should now be possible but had not yet been demonstrated at the time of this report.

Benefits to DOE

A fully dynamic, integrated NHES simulation platform provides the tools necessary to analyze candidate hybrid system architectures, formulate associated value propositions for leading NHES architectures, and identify a feasible path forward to closing key technology gaps. Realization of the NHES architecture crosscuts DOE Nuclear Energy, Energy Efficiency and Renewable Energy, and Fossil Energy interests, potentially providing more efficient and reliable integrated energy systems.

Relevant Publications and Presentations

Bragg-Sitton, S. and J.M. Doster, "Model Development for Transient Performance Analysis of a Small Modular Reactor in a Hybrid Energy System," *INL INEST Advisory Board, Idaho Falls, ID, September 18, 2012*.

CENTER FOR
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Optimization of Ceramic Waste Forms Used for Electrochemical Processing of Spent Nuclear Fuel

Michael Simpson, Supathorn Phongikaroon,[1] Ammon Williams,[1] Joshua Versey,[1] Man-Sung Yim,[2] and James Allensworth[2]

10-015

Pyroprocessing is a promising technology for recycling used nuclear fuel and improving associated waste management options. This project aimed to develop technology to minimize the volume of high-level nuclear waste generated from pyroprocessing. Fission products from the used fuel accumulate in molten salt electrolytes during electrochemical treatment of the fuel. Excessive concentrations of these fission products in the base salt (LiCl or LiCl-KCl) necessitates either purifying or disposing of the salt. Simply disposing of the salt can result in relatively high volumes of waste. Alternatively, separations processes can be applied to the salt to extract or concentrate the fission products. Zone freezing, for example, has been shown to result in formation of a solid salt layer concentrated in the fission products and another layer that is relatively pure salt (LiCl or LiCl-KCl). This can potentially lead to recycling of purified salt and up to an 80% reduction in the volume of salt waste. This project sought to understand the fundamental processes governing phase separation of molten chloride salts to enable the development of predictive models and process optimization. Methods for immobilizing the concentrated salt product were developed consistent with conversion into robust waste forms, specifically involving first sorption into a zeolitic molecular sieve. Ultimately, by combining optimized salt freezing with optimized salt sorption by zeolites, it is predicted that the volume of high-level waste can be reduced by a factor of five or more compared to baseline pyroprocessing waste technology. This would greatly improve the viability of pyroprocessing as a commercial process.

Summary

This project supported three separate graduate student projects to study key technical aspects of the overall problem of optimization of ceramic waste forms from electrochemical processing of spent nuclear fuel. Those student projects were as follows.

- Zone freeze refining for recycle of LiCl-KCl from contaminated electrorefiner salt (University of Idaho)

- Diffusion and absorption of LiCl-KCl with high concentrations of fission product chlorides in zeolite-A (North Carolina State University)

- Recycle of LiCl from contaminated oxide reduction salt using a cold finger (University of Idaho).

Zone Freeze Refining (with the University of Idaho). Experiments were performed to study the phase separation of LiCl-KCl based electrorefiner salt as a result of slowly moving a salt sample through a furnace from a hot zone to a cold zone. The hot zone was set above the melting point of the salt, while the cold zone was cooler than the melting point. Based on results published by the Korea Atomic Energy Research Institute, it was expected that two solid layers would form—including a fission product rich layer and a purified LiCl-KCl layer. Most experiments involved salt containing initially 2 wt% CsCl. Process conditions were varied with optimal conditions found to include a 5 mm/hr translation rate, a lid covering on the crucible, and a temperature difference of $200^{o}C$ between the hot and cold zones. It was found to be possible to separate 86% of the LiCl-KCl in the purified layer, with the remaining CsCl concentrated up to 9 wt%. A model was also developed to better understand the observed experimental results. While it was demonstrated that zone freezing could be used to significantly lower the amount of ceramic waste from pyroprocessing, the slow translation rates would make it unlikely that this process could be cost effectively scaled up.

Cold Finger Separation (with the University of Idaho). Experiments were performed to study the solidification of LiCl on a cooled metal tube inserted into molten LiCl-CsCl. The application for this study is the recycle of LiCl from contaminated salt used for electrolytic reduction of oxide fuel. Cesium and other Group I and II fission products from the spent fuel will partition into the molten salt during this reduction process. Eventually, the salt becomes too contaminated to continue to be used for the reduction process. If it was possible to selectively extract LiCl from the salt, it could be recycled and the remaining salt would then be concentrated in the ceramic waste form. The ultimate outcome would be minimization of ceramic waste volume. In the experiments performed in this study, argon gas flowed through the tube (cold finger) and was used to reduce its temperature relative to the bulk molten salt that was maintained at $650^{°}C$. Salt crystals were observed to grow on the cold finger during the process. Effect of gas flow rate and growth time was studied in an attempt to determine the optimal process conditions. In small-scale experiments, up to 0.36 g of salt per min growth rate was

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achieved on a single cold finger. Samples of the crystals were dissolved and analyzed via inductively coupled plasma mass spectrometry. While the initial salt included 5 wt% CsCl, under the optimum growth conditions the crystal contained only 0.33 wt% CsCl. A montage of pictures of the salt crystals deposited on the cold finger is shown in Figure 1.
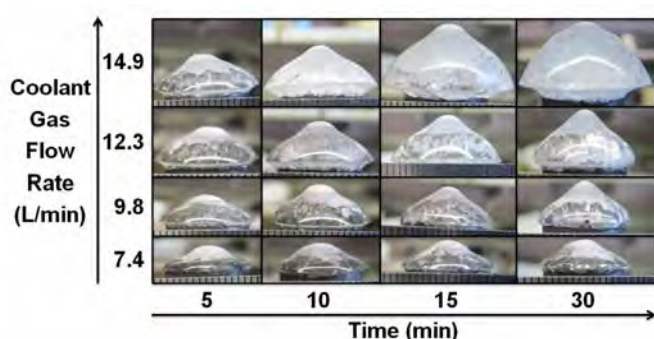

FIGURE 1. Salt Crystals Formed on a Cold Finger (with University of Idaho).

Salt Diffusion and Absorption in Zeolite-A. Experiments were performed to study the sorption properties of various chloride salts in zeolite-A. In the baseline pyroprocessing flowsheet, waste salt containing primarily LiCl-KCl is absorbed by zeolite-A and thermally converted into a sodalite-based ceramic waste form. This sorption process is largely facilitated by the low melting point of LiCl-KCl such that the salt becomes molten and readily diffuses into zeolite particles and crystals. Removal of LiCl-KCl or LiCl using methods such as those studied in this project could effectively prevent waste salt from melting during the zeolite sorption process. Solid-state diffusion would need to occur for the fission product chlorides to effectively be sorbed by the zeolite. In this study, it was shown that pure salts such as CsCl, RbCl, SrCl2, etc., do in fact absorb into the zeolite with little to no LiCl-KCl present. Experiments were performed with both salt powders and molten salts to investigate the mechanisms and fundamental limitations of the process. The process was found to be diffusion limited. A particle diffusion model was fit to the data, and diffusion coefficients for CsCl and SrCl2 in the zeolite particles were determined. The end results included confirmation that LiCl-KCl is not needed to facilitate fission product chloride sorption in the zeolite, and a predictive kinetic model is now available to support further process analysis.

This project contributed to building a national laboratory-university team for achieving key DOE objectives. It engaged three universities (the University of Idaho, Idaho State University, and North Carolina State University) in INL research at CAES. This helps demonstrate how INL can further its mission via strategic partnerships facilitated by CAES.

Benefits to DOE

This project benefits DOE's energy security mission by supporting the closing of the nuclear fuel cycle, potentially making nuclear energy sustainable with minimal environmental impact. The project has been successful in demonstrating a viable salt purification method (solidification on a cold finger) and a process for immobilizing the residual salt waste into a waste form (solid state sorption in zeolite-A). Models are available for both the salt purification and sorption processes to aid in future analysis and evaluation of technologies. Overall, this project has provided the tools to enable serious consideration of a novel and potentially economical waste process.

Relevant Publications and Presentations

Williams, A.N., S. Phongikaroon, and M.F. Simpson, "Separation of CsCl from a Ternary CsCl-LiCl-KCl Salt via a Melt Crystallization Technique for Pyroprocessing Waste Minimization," *Chemical Engineering Science.* (submitted)

Allensworth, J.R., M.F. Simpson, M.S. Yim, and S. Phongikaroon, "Investigation of Fission Product Transport into Zeolite-A for Pyroprocessing Waste Minimization," *Nuclear Technology.* (in press)

Allensworth, J.R., M.S. Yim, and M.F. Simpson, "A Study of Highly Concentrated Fission Product Salt Loading into Zeolite-A," *Proceedings of GLOBAL 2011, Makuhari, Japan, December 11-16, 2011.*

Williams, A.N., S. Phongikaroon, and M.F. Simpson, "Zone Freezing Model for Pyrochemical Process Waste Minimization," *2010 Annual Meeting of the American Institute of Chemical Engineers,* Salt Lake City, Utah, *November 7-12, 2010.*

Simpson, M.F., J.R. Allensworth, M.S. Yim, M. Shaltry, S. Phongikaroon, C. Ferguson, and M.L. Dunzik-Gougar, "Immobilization of Salt from Zone Freezing Process in Zeolite-A," *2010 International Pyroprocessing Research Conference, Dimitrovgrad, Russia, November 29–December 3, 2010*.

Williams, A.N., S. Phongikaroon, and M.F. Simpson, "Zone Freezing Study for Pyrochemical Process Waste Minimization," *Center for Advanced Energy Studies Colloquium Series, April 2011*.

Simpson, M.F., M.S. Yim, M. Lineberry, M.L. Dunzik-Gougar, A.N. Williams, M. Shaltry, D. LaBrier, J.R. Allensworth, R. Bezzant, C. Ferguson, and J. Wallis, "Developing Chemical Separations Methods to Minimize High Level Waste from Pyroprocessing of Spent Nuclear Fuel," *Center for Advanced Energy Studies Colloquium Series, August 31, 2011*.

Williams, A.N., S. Phongikaroon, and M.F. Simpson, "Separation of CsCl from Ternary CsCl-LiCl-KCl Salt via a Zone Freezing Method," *American Nuclear Society Winter Meeting, Washington, D.C., October 30–November 3, 2011*.

Williams, A.N., S. Phongikaroon, and M.F. Simpson, "Zone Freezing Study for Pyrochemical Process Waste Minimization," *2012 International Pyroprocessing Research Conference, Fontana, Wisconsin, August 26–29, 2012*.

Versey, J.R., S. Phongikaroon, and M.F. Simpson, "Fission Product Separation by Cold Finger Crystal Growth," *2012 International Pyroprocessing Research Conference, Fontana, Wisconsin, August 26–29, 2012*.

Small Specimen Test Techniques for Evaluating Radiation-Induced Changes in Mechanical Properties

Bulent Sencer, Mitchell Meyer, Darryl Butt,[1] and Frank Garner[1]
10-024

This project demonstrates the reliability of engineering data produced from tensile and shear-punch tests on small radioactive samples that can be handled behind light shielding or in fume hoods. Capabilities developed for this project include an enclosed and HEPA-vented shear punch and mini tensile tester, a modified drop tower to perform tests on small Charpy samples, and a micro-density device to measure the post-irradiation swelling of 3-mm discs. Such radioactive material as stainless steels and oxide-dispersion strengthened steels were tested including ferro-probe measurements on shear-punched stainless steels to test for martensitic phase transformation due to deformations. In addition to tensile and shear punch tests, nondestructive (electro-resistive and ultrasonic) tests were performed to study void swelling, transmutation and other radiation-induced property changes of small specimens. An integral part of this testing regime was examination by electron microscopy before and after testing.

A secondary objective of this project was to engage university students and faculty and demonstrate that such teams can produce useful engineering data on the physical and mechanical properties of nuclear materials without the necessity of using a hot cell. In addition to providing reliable engineering data, this project provides the safety basis for conducting such experiments with radioactive materials in a university environment.

Summary

Equipment was acquired including an Instron tensile test station equipped with high temperature grips, a furnace, two anvils, and a Linear Variable Differential Transformer. An enclosure was fabricated for this system and its performance validated regarding heat and radioactivity. Also, a commercial drop tower was modified to perform shear punch and tensile tests as well as Charpy tests. In addition, a micro density measurement cell was manufactured, assembled, and validated. To study

deformation and strain effects on 304 stainless steel, tests were performed on ATR-irradiated oxide dispersion-strengthened steel, five shear punch discs from MFC, and a number of shear punch discs from Westinghouse. Both irradiated and un-irradiated samples were included. The development and validation of this test capability in a university environment is generating substantial enthusiasm for this approach. Two pre-proposals have been submitted to fund further work on this apparatus.

Benefits to DOE

This project supports life extension of the current fleet of Light Water Reactors and development of new materials for the next generation of reactors. This project comes at a time when it is critical to provide opportunities and training for a new generation of radiation materials scientists to enable continued use of nuclear energy in the U.S. as a clean, reliable energy source. The graduate student supported by this project successfully completed an M.S. degree and is now working as a material scientist for National Aeronautic and Space Academy.

Relevant Publications and Presentations

Rabenberg, E.M., K. Knori, B.J. Jacques, B.H. Sencer, Y. Huang, F.A. Garner, and D.P. Butt, "Small Specimen Testing for Evaluating Radiation-Induced Changes in Mechanical Properties of Structural Reactor Materials at High Radiation Doses," *Presented at the 141st Annual TMS 2012 Conference, Orlando, FL, March 11-15, 2012.*

Rabenberg, E.M., K. Knori, B.J. Jaques, B.H. Sencer, F.A. Garner, P.D. Freyer, and D.P. Butt, "Influence of Irradiation Damage and Temperature on the Strength of 304SS," *Journal of Nuclear Materials*, 2013. (submitted)

Rabenberg, E.M., "Small Specimen Test Techniques for Evaluating Radiation-Induced Changes in Mechanical Properties," M.S. Thesis, Boise State University, 2012.

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Prediction and Monitoring of CO$_2$ Behavior in Deep Reactive Geologic Formations

Travis McLing, Robert Podgorney, Jerry Fairley,[1] and Kasper van Wijk[2]
10-053

The primary obstacle to sequestering carbon dioxide in geologic repositories (as an alternative to releasing carbon dioxide into the atmosphere) is the cost of such systems. Reducing the cost of potential geological sequestration efforts will require a unique blend of modeling and geology knowledge. To this end, this project was a cooperative effort between the INL, Boise State University, and the University of Idaho, with each of the organizations providing a very specific skill set that is needed to help bridge the large knowledge gap associated with the characterization of reactive rocks (specifically the mafic rocks of Idaho and the Pacific Northwest) for potential CO$_2$ storage. The field characterization and modeling activities were lead by the University of Idaho and INL, while the geophysics modeling and experiments were lead by Boise State University. Additionally, with the help of CAMS, INL completed a large-scale digital elevation model model of the geologic gram work.

We examined the potential for sequestering waste carbon dioxide in the deep, fractured basalts of the Eastern Snake River Plain (ESRP). In order to safely and economically sequester waste carbon dioxide in the ESRP, the long term injectivity of the basalts must be sufficient to accept economic quantities of "liquefied" (supercritical) carbon dioxide, and the carbon dioxide must not migrate to shallower aquifers containing potable water supplies. Typically, characterizing geologic carbon dioxide sequestration reservoirs is extremely costly as a result of the large number of wells required to understand the geometry and size of the reservoir. An additional objective of this study was to find an economical alternative to the installation of a large number of wells when seeking a target injection zone.

This project completed its goals. Additionally, as a result of the increased understanding and ability to model basaltic systems, National Aeronautic and Space Administration has expressed interest in conducting several propulsion tests at INL. The PI is currently working to identify the work scope and project objective.

Summary

Geophysics—To study the feasibility of using seismic methods to monitor rock property changes in CO$_2$ sequestration in basalt, we performed elastic wave laboratory experiments on basalt core at reservoir conditions. We quantified the elastic and physical property variations for basalt rocks exposed to CO$_2$ and water. When CO$_2$ is injected into a water-saturated basalt, two elastic wave propagation effects are expected: (1) the P-wave velocity decreases as water is substituted by CO$_2$, a more compressible fluid, and (2) P- and S- wave velocities increase as minerals form in cracks and pores due to the fluid-rock reactions in the presence of carbonic acid. Although theoretically these are the expected changes in wave velocity, there have not been any previous studies on elastic rock properties in basalts with CO$_2$ and on real time mineralization on whole basalt core. At ultrasonic frequencies and at a differential pressure of 17.2 MPa (depth of 1 Km), we measure a 10% decrease in velocity due to CO$_2$ substituting water, but at seismic frequencies (2-100 Hz) we observe a velocity decrease between 3% and 10%. The amount of change results from the frequency dependent velocity when basalt cores are saturated with water. Larger elastic changes due to fluid substitution are measured for the bulk modulus, with an average change of 30%.

The water and CO$_2$-saturated rock bulk modulus is modeled with two rock physics theories. For the three measured samples, Gassmann's theory predicts the measured data at frequencies lower than 20 Hz, but under predicts ultrasonic modulus measurements. Kuster-Toksöz, an elastic theory developed for high frequencies, predicts the ultrasonic measured bulk modulus when rock analysis on pore distribution and shapes is incorporated into the computations. The differences in measured elastic properties with frequency and pressure are directly related to the amount of open cracks and compliant pores in these rocks.

To estimate the effects of carbonate precipitation on elastic properties, the basalt samples are placed in a reactor vessel at reservoir conditions to instigate mineralization. Wave velocity on dry basalt samples is measured with a laser ultrasonic system before reactions occur and at two reaction time intervals: 15 and 30 weeks. P-wave velocity estimated from direct arrivals increases on average by 6.7% for the first 15-week measurement and an average change of 7.8% from 15–30 weeks. When analyzing the data with coda wave interferometry the basalt shear wave velocity increases on average by 1.8%

from 0–15 weeks and 1.9% from 15–30 weeks. Fluid transport and storage properties both decreased, which supports the observation of an increase in velocity. For two of the samples, porosity decreased from 18.08% to 17.28%, and from 15.16% to 13.03%. Permeability was reduced significantly from 1.12 mD to 0.32 mD, and from 1.32 mD to 0.09 mD, on average a decrease of 85%.

Mineral precipitate is observed in a variety of pore shapes and sizes from 3-D CT-scan images and thin sections. We observe carbonate precipitation (possibly with iron and magnesium composition) from analyzing vesicles and crack walls in these images. From petrography, we interpret that the glassy groundmass is the source of dissolution, as mineral crystals are not altered after 30 weeks of reaction. Water chemistry and geochemistry also show the dissolution and precipitation process in these basalts. The amount of mineral volume of the total rock that the precipitate represents is less than 3%. However, many carbonate crystals grew in cracks and compliant pores, thus blocking fluid flow and stiffening the rock to the passing elastic wave.

Although basalt flows are difficult to image with seismic methods, previously modeled time-lapse changes from coda waves in layered basalt were able to resolve a 5% velocity change. Because the velocity data reported in this work for fluid substitution and mineral precipitation are equal or greater to 5%, we conclude that field-based seismic methods can potentially monitor fluid and rock changes in a basalt reservoir. This work also contributes information for developing the use of elastic waves to monitor rock alterations in CO_2-water environments present in other geologic settings such as active volcanoes, mid-oceanic ridges and geothermal reservoirs.

Geostatistical modeling—We collected extensive data on fractures in basalts to construct statistical models of potential waste carbon dioxide reservoirs at depths below the shallow potable aquifer of the ESRP. We then used these hypothetical reservoirs to develop numerical models to test possible carbon dioxide injection schemes.

Our modeling resulted in three important inferences regarding the potential for carbon dioxide sequestration in the ESRP. First, there is a very high probability that injection wells completed in the deep, lower-permeability fractured basalts underlying the shallow aquifer of the ESRP will intersect high-permeability zones that would constitute potential targets for sequestration of waste carbon dioxide. Second, our modeling indicates that greater than 50% of the potential target horizons identified by drilling should be able to accept long-term (>10 years) waste carbon dioxide injection at rates of ~21.6 kg/s (equivalent to about half the output of a 1000 MW coal-fired power plant). Third, apparently high-permeability zones that were not suitable long-term injection targets failed because of pressure buildup over reasonably short timeframes (e.g., 6 months). As a result, a target interval can be tested with a relatively inexpensive water injection test lasting on the order of 6 months. Although such a test is time consuming when compared to industry standard aquifer tests (which typically last on the order of days), a 6-month aquifer stress test is cheap in comparison to the installation of a large number of characterization wells or the construction and outfitting of a carbon dioxide injection well that fails due to pressure buildup after 6 months or a year of operation.

This LDRD project represents an ideal model for effective team building between a national laboratory (INL) and the CAES university partners. Over the life cycle of the project four Masters of Science degrees and one Ph.D. were earned as a result of the support provided through the CAES Geofluids LDRD. Degrees were earned in geosciences through collaboration with all three Idaho CAES partnering institutions. Several of these students and their faculty advisors were actually located during the summer at the CAES building. These relationships continue to foster additional research opportunities for CAES supporting the INL mission. Most importantly, the students educated and trained through this research project have moved on to permanent employment supporting the energy sector in the U.S.

Benefits to DOE

The results of this project are important for energy security offering the potential for relatively inexpensive waste carbon dioxide sequestration when paired with next-generation coal-fired power plants capable of separating carbon dioxide from flue gases. The project outcomes also offer the possibility of economically supportable carbon dioxide sequestration for small- to medium-sized emitters that could not otherwise afford to develop and maintain a geologic sequestration reservoir. Furthermore, the State of Idaho may be able to use the study findings for economic development, because the

results indicate that the basalts of the ESRP are likely to be suitable for construction of low-cost geologic carbon sequestration reservoirs (and thus reservoir space may be sold or leased by the State of Idaho or by private companies licensed by the State of Idaho).

Relevant Publications and Presentations

Otheim, T., "Monitoring CO_2 Sequestration in Basalt With Elastic Waves," Master's Thesis, Boise State University, 2012.

Adam, L., K. van Wijk, M. Batzle, T.L. McLing, and R. Podgorney, "CO_2 Sequestration in Basalts: Fluid Substitution and Carbonate Mineralization," *The Leading Edge,* Vol. 30, 12, 2011.

Khatiwada, M., L. Adam, M. Morrison and K. van Wijk, "A Feasibility Study of Time-Lapse Seismic Monitoring of CO_2 Sequestration in a Layered Basalt Reservoir," *The Journal of Applied Geophysics*, Vol. 82, 2012.

Adam, L. and T. Otheim, "Elastic Laboratory Measurements and Modeling of Saturated Basalts'" Under review in *Journal of Geophysical Research,* 2012.

Adam, L., T. Otheim, K. van Wijk, and M. Batlze, "Monitoring Carbonate Precipitation in Basalt from Reactions with Carbonic Acid," 2013. (in preparation)

Adam, L., P. Olin, C. White, and T. Otheim, "Carbonic Acid – Basalt Reactions on Whole Core," 2013. (in preparation)

Adam, L. and T. Otheim, "Frequency Dependent Elastic Properties and Attenuation in Basalt," 2013. (in preparation)

Pollyea, R.M., J.P. Fairley, R.K. Podgorney, and T.L. McLing, "Developing a Field Sampling Strategy for Continuum Representation of Fractured Rock Using Outcrop Analogs," *Ground Water Monitoring and Remediation,* 2011. (submitted)

Pollyea, R.M. and J.P. Fairley, "Implications of Reservoir Uncertainty for CO_2 Sequestration in Low-Volume Basalt," *Hydrogeology Journal*, doi:10.1007/s10040-012-0847-1, 2012.

Pollyea, R.M. and J.P. Fairley, "Experimental Evaluation of Terrestrial LiDAR-Based Surface Roughness

Estimates," *Geosphere*, Vol. 8, 1, doi:10.1130/GES00733.1, 2012.

Pollyea, R.M. and J.P. Fairley, "Estimating Surface Roughness of Terrestrial Laser Scan Data Using Orthogonal Distance Regression," *Geology*, 39(7):623-626, doi:10.1130/G32078.1, 2011.

Pollyea, R.M., "Implications of Fracture Heterogeneity for Geologic Carbon Sequestration in a Reactive Basalt Aquifer," Ph.D. Dissertation, University of Idaho, 2012.

Pollyea, R.M. and J.P. Fairley, "Numerical Modeling Experiment Reveals Opportunities and Challenges for CO_2 Sequestration in Low-Volume Basalt Formations," *GSA Annual Meeting, Paper 52-T88 (oral), 2012*.

Pollyea, R.M. and J.P. Fairley, "Implications of Reservoir Uncertainty for Geologic Carbon Sequestration in Low-Volume Basalt Flows," *AGU Annual Meeting, H24B-06 (oral), 2011*.

Pollyea, R.M. and J.P. Fairley, "Evaluating Errors in Least-Squares Based Surface Roughness Models for Analyzing Terrestrial LiDAR Data," GSA Annual Meeting, Paper 48-10 (oral), 2011.

Pollyea, R.M., J.P. Fairley, R.K. Podgorney, and T.L. McLing, "Developing Fracture Density Models Using Terrestrial Laser Scan Data," *AGU Annual Meeting, San Francisco, CA (oral), 2010*.

Pollyea, R.M., J.P. Fairley, R.K. Podgorney, and T.L. McLing, "Simulation Heterogeneous Property Distributions for Carbon Dioxide Injection Modeling in Fractured Basalts," *Geological Society of America Annual Meeting, Portland, OR, 2009*.

Fairley, J.P., R.M. Pollyea, R.K. Podgorney, T.L. McLing, and R. Smith, "Testing CO_2 Isolation with Synthetic Models of Heterogeneous Layered Basalt," *5th Trondheim Conference on CO_2 Capture, Transport and Storage, Trondheim, Norway, 2009*.

Pollyea, R.M. and J.P. Fairley, "Using Geostatistical Methods to Inform Field Sampling of Heterogeneous Fractured Media (Poster H41A-0841*)," American Geophysical Union Fall Annual Meeting, San Francisco, CA, 2008*.

Podgorney, R.K., T.L. McLing, and J.P. Fairley, "Optimizing Injection Strategies for Supercritical CO_2 Injection into Mafic Rocks," *CO_2 Capture and Sequestration Workshop, Pittsburgh, PA, 2007.*

Fairley, J.P., "Assessing the Feasibility of CO_2 Sequestration in a Fractured Basalt Reservoir," *Utah State University Department of Geology Distinguished Lecturer Series, 2012.*

Fairley, J.P., "The Potential for CO_2 Sequestration in Idaho's Deep Basalts," *University of Idaho Environmental Science Seminar, 2012.*

Fairley, J.P., "Assessing the Feasibility of CO_2 Sequestration in a Fractured Basalt Reservoir," *University of Idaho Department of Plant, Soil, and Entomological Sciences Seminar, 2012.*

Otheim T., L. Adam, K. van Wijk, M. Batzle, T.L. McLing and R.K. Podgorney, "Geophysical Signatures to Monitor Fluids and Mineralization for CO_2 Injection in Basalts," *AGU Fall Meeting, San Francisco, CA, 2011.*

Adam L., T. Otheim, K. van Wijk, M. Batzle, T.L. McLing, and R.K. Podgorney, "CO_2 Sequestration in Basalt: Carbonate Mineralization and Fluid Substitution," *SEG Annual Meeting, San Antonio, TX, 2011.*

Adam, L., T. Otheim, K. van Wijk, M. Batzle, T.L. McLing, and R.K. Podgorney, "Basalt, Fluids and Laboratory Techniques," *International Rock Physics Workshop, Golden, CO.*

Otheim T., L. Adam, K. van Wijk, T.L. McLing and R.K. Podgorney, "CO_2 Sequestration in Basalts: Laboratory Measurements," *AGU Fall Meeting, San Francisco, CA, 2010.*

Fabrication of Advanced ODS Alloys Using Field-Assisted Sintering

James Cole, Larry Zirker, Indrajit Charit,[1] Darryl Butt,[2] and Kerry Allahar[2]
10-056

In order to retain adequate strength at the elevated temperatures being considered for many of the advanced nuclear reactor system designs, new alloys with dispersions of nanometer scale oxide particles (oxide dispersion-strengthened or ODS) are being developed. Oxide dispersions provide enhanced resistance to creep deformation and have also been found to increase resistance to radiation damage. Conventional methods of producing these materials involve complex and costly powder metallurgy production methods. We assessed the use of spark plasma sintering or field-assisted sintering (FAS) as a means for eliminating hot extrusion and hot pressing (intermediate ODS-processing steps) thus simplifying ODS production and potentially reducing costs. FAS also reduces anisotropy produced during extrusion, a significant limitation of conventional processing when producing tubing for nuclear fuel cladding applications. FAS has been commercially developed in Japan for processing of a wide range of engineering materials and has a number of attractive features unavailable from conventional processing methods. However, FAS has never been applied to processing ODS alloys nor have the unique materials issues (both scientific and technical) been explored. One major advantage of FAS that has been exploited to great benefit in this effort is the ability to rapidly produce samples for testing and characterization, allowing the systematic variation of alloy composition and processing parameters to optimize material properties.

Summary

New ODS alloy composition for fuel cladding applications for the next generation nuclear reactors were designed based on a ferritic matrix and high chromium content. The alloy's constituents were fabricated (both at Boise State University and the University of Idaho) and consolidated using the FAS system located at CAES. The fabricated alloys were then characterized in detail using advanced microscopy techniques available in the CAES Microscopy and Characterization Suite (MaCS) laboratory (scanning and transmission electron microscopy [TEM] and local electrode atom probe tomography [LEAP]).

The alloy fabrication development effort successfully demonstrated that fabrication of ODS alloys is possible using FAS as the consolidation technique. The obtained microstructures have nanograins with higher hardness and strength due to lower sintering temperature and shorter sintering time than conventional processing. Mechanical properties and microstructural characteristics of newly developed ODS alloys with La_2O_3 additive have shown higher hardness compared to the same composition with Y_2O_3 additive, confirming La_2O_3 as a promising alternative for Y_2O_3. Microstructural characterization using TEM and LEAP confirmed the presence of high densities or uniformly distributed nanoscale oxide particles in the material, comparable to conventionally-processed alloy microstructures. An example of the microstructure in the lanthana-bearing alloy is shown in the TEM micrograph of Figure 1. These extremely fine particles impede dislocation mobility at high temperature and act as trapping sites for point defects during irradiation—providing enhanced creep strength and radiation resistance.
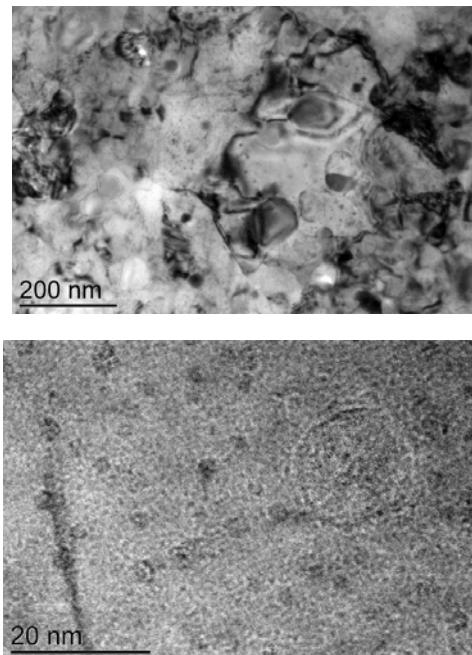
FIGURE 1. (Top) Bright field TEM image of 14 LMT sintered at 950°C for 45 minutes showing nanograins; (bottom) HRTEM image showing Cr-Ti-La enriched oxides as small as 2 nm.

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[1] University of Idaho

[2] Boise State University

In addition to FAS fabrication development, efforts were conducted to investigate an advanced solid state welding method for joining ODS alloys for fuel pin applications as conventional fusion welding options cannot be used with ODS alloys due to destruction of the uniform oxide particle distribution during the welding process. ODS tubing was joined with high Cr steel end-plugs using a pressure resistance welding system installed in CAES. The system successfully produced crack and void free joints with greater strength than either of the parent materials. The effort was formally documented in an INL external report.

This research directly facilitated development of state-of-the-art research capabilities and technical expertise at CAES, engaging two Idaho universities, creating opportunities for graduate students and other research personnel in their educational/training activities and supporting advanced fuel cladding development.

Benefits to DOE

ODS clad oxide fuels can potentially improve safety margins and efficiency in current commercial nuclear reactors and dramatically improve fuel cladding performance of more advanced nuclear reactor systems envisioned for future deployment. This is due to ODS clad fuels improved mechanical properties and resistance to deleterious radiation effects such as void swelling. Research using the FAS for ODS steels is relatively novel. As a result, INL and its university partners are well positioned to lead future efforts to exploit this technology for further ODS alloy development as well as novel nuclear fuel development.

Relevant Publications and Presentations

Allahar, K., J. Burns, B. Jaques, I. Charit, D.P. Butt, and J. Cole, "Spark Plasma Sintering of Ferritic Oxide Dispersion Strengthened Alloys," *Processing and Properties of Powder-Based Materials*, 2011 TMS *Annual Meeting & Exhibition, San Diego, CA, March 2011.*

Jerred, N., L. Zirker, B. Jaques, T. Bradshaw, J. Carrillo, E. Young, I. Charit, J.I. Cole, M. Frary, D.P. Butt, M. Meyer, and K.L. Murty, "Pressure Resistance Welding of High Temperature Metallic Materials," *Joining of Advanced and Specialty Materials XII, Materials Science and Technology 2010, Houston, TX, October 17–21, 2010.* (accepted)

Jerred, N.D., L. Zirker, I. Charit, J. Burns, Y.Q. Wu, and J.I. Cole, "Pressure Resistance Welding of HT-9 End-Plugs to Fast-Reactor Oxide Dispersion Strengthened Cladding Tubes," *NuMat 2012 (Nuclear Materials Conference), Osaka, Japan, October 2012.*

Pasebani, S., I. Charit, D.P. Butt, and J.I. Cole, "Effect of Ball Milling Time on the Lanthana Containing Nanostructured Ferritic Steels," *Journal of Nuclear Materials,* 2012. (submitted)

Pasebani, S., I. Charit, K. Allahar, J.I. Cole, and D.P. Butt, "Oxide Dispersion Strengthened Steels via Mechanical Alloying and Spark Plasma Sintering," *Materials and Fuels for the Current and Advanced Reactors*, TMS *Annual Meeting, Orlando, Florida, May 11–15, 2012.*

Pasebani, S., I. Charit, K. Allahar, B. Jaques, D.P. Butt, and J.I. Cole, "Development of Oxide Dispersion Strengthened Steels via Mechanical Alloying and Spark Plasma Sintering," *Energy Materials Symposium, Thermec 2011, Quebec City, Canada, August 1–5, 2011.* (invited)

Pasebani, S., I. Charit, K. Allahar, B. Jaques, D.P. Butt, J.I. Cole, "Microstructural Characterization of Mechanically Alloyed Lanthana Bearing Oxide Dispersion Strengthened Steels," *Processing and Properties of Powder-Based Materials*, TMS Annual *Meeting, San Diego, CA, February 28–March 3, 2011.*

Transmission Site Suitability Decision Support Technology

Jeffrey Joe, David Solan,[1] David Koehler,[1] Robert Beazer,[2] Juliet Carlisle,[2] Daniel Ames,[2] and Stephanie Kane[3]
10-079

New overhead high-voltage electricity transmission lines must be built to meet increasing demand. To address this need, utility companies and planners typically use geographic information system (GIS)-based software tools to help characterize the landscape the transmission lines must traverse. This is because the physical landscape and regulatory constraints that affect line placement can be treated as a spatial optimization problem. Specifically, GIS techniques optimize the placement of transmission lines by converting geospatial information (e.g., terrain) into rasters of constraint feature layers, apply layer weightings through map algebra, and in the case of transmission line siting, optimize the spatial constraints using least-cost path analysis. Since developers typically submit proposals for transmission line corridors that are least-cost based on technical and geospatial considerations, this GIS-based problem solving approach has proven useful. However, due to utility companies' acknowledged lack of understanding regarding public opinion and participation in siting decisions, initial proposals of where transmission lines should be placed often miss the mark with the public and create severe opposition.

To address the need for better electric transmission planning tools, this project developed an open source prototype GIS-based decision support tool called LineSiter. LineSiter facilitates electric transmission line route selections by integrating geospatial data with public opinion and other socio-political constraint information. The result of this integration is an innovative GIS siting and visualization tool that more effectively performs least-cost path analyses to identify optimal transmission corridors.

Summary

At the end of FY 2012, the project accomplished all internal project goals set for this three-year LDRD project. For the GIS software, the project software developers gathered and organized geospatial data sets, worked with the rest of the team to develop a theoretical model for how the tool would use a Monte Carlo simulation analysis approach to integrate the socio-political data, wrote the computer code for the GIS tool, wrote the user's guides for the software, and tested the GIS tool and the Monte Carlo approach to integrating socio-political with geospatial data in a case study. The survey team formulated questions that identified and measured levels of opposition and other socio-political constraints, issued the survey, analyzed the survey results, and assisted in the integration of the survey data into the GIS-based tool.

The development of the Monte Carlo simulation was one of the key technical accomplishments for this LDRD. One goal was to use entire frequency distribution of responses from the public to key survey questions, such that a more complete representation of the range of public opinions about siting electrical transmission lines could be integrated into the GIS tool. In order to accommodate the use of the response frequency distributions, Monte Carlo simulation was used. The Monte Carlo simulation performed random sampling of the response frequency distributions to determine how much weight public opinion would have in affecting the utilities' geospatially defined costs, combined that weighted public opinion with the geospatially defined costs, and then calculated the least-cost path for the transmission line in question.

Because the random sampling of the frequency distributions can be done repeatedly, the Monte Carlo simulation also gives LineSiter the ability to generate multiple least-cost paths, depending on the outcome of the Monte Carlo simulation (i.e., the amount of weight public opinion has for a given iteration of the simulation). This capability to generate multiple least-cost paths is beneficial, as it can show how different least-cost paths can occur depending on the degree to which public opinion is considered, and/or by how much weight certain aspects of public opinion are given. This multiple least-cost path generation would not be possible if a deterministic approach were used instead of Monte Carlo simulation, as a deterministic approach would always produce the same output, given a particular input from the survey.

The end product of these efforts is LineSiter, an open source GIS-based tool that facilitates utility companies' ability to consider socio-political constraints along with geospatial constraints from the outset of the siting process as a way to avoid the potential pitfalls that come from doing otherwise. LineSiter is available to the public for free and can be downloaded at: http://linesiter.codeplex.com.

[1] Boise State University

[2] Idaho State University

[3] University of Idaho

The multi-institutional research team submitted a proposal to the DOE SunShot initiative, which is a collaborative national initiative and funding grant to make solar energy technologies cost-competitive with other forms of energy, and was awarded $2.8M to develop a GIS decision support tool to identify utility-scale solar facility sites based on quantifiable natural resource and physical constraints, as well as a scientific measure of social risk and public acceptance of screened sites. This SunShot project is scheduled to run for three years, and advances the deployment of secure and sustainable energy systems. In addition, project team member Robert Beazer was the primary author and developer of LineSiter. As a result of his work, including the innovative integration of Monte Carlo simulation in the GIS tool, Robert earned his Ph.D. in Geosciences from Idaho State University. In doing this research, Robert has also developed energy domain-specific knowledge and skills that are critical to the successful completion of numerous DOE missions.

Benefits to DOE

Through effective collaboration on this LDRD, the INL and state universities in Idaho gained critical technical knowledge and experience that allowed them to address the challenges of siting energy infrastructure.

This research has and will continue to improve INL's considerable subject matter expertise in the areas of electric transmission siting, utility scale solar facility siting, GIS software development, and energy policy. Project team members have already made numerous conference presentations, and are working on publishing a number of papers in peer-reviewed journals.

Finally, the resulting GIS tool facilitates transmission line siting decisions. In doing so, this GIS tool provides cost savings to public and private entities, minimizes environmental impacts of transmission line siting, minimizes the risk of transmission project failure due to technical and socio-political factors, and strengthens our national security through enhancing our critical energy infrastructure.

Relevant Publications and Presentations

Beazer, R., "Integrating Social Attitudes, Spatial Data, and Monte Carlo Simulation Modeling for Siting of High Voltage Power Lines," *A dissertation completed for the degree of Doctor of Philosophy in Engineering and Applied Science in the College of Science and Engineering at Idaho State University.*

Carlisle, J., J. Joe, D. Solan, D. Ames, and R. Beazer, "Public Reactions to Electric Transmission Line Siting: The Role of Nimbyism vs. Environmentalism," *Environmental Politics,* 2012. (in review)

Ames, D. and R. Beazer, "Integrating Social Attitudes and Spatial Data in Siting Power Lines Using the DotSpatial Framework," *2nd International MapWindow GIS and DotSpatial Conference 2011, San Diego, CA, June 2011.*

Beazer, R., "Utility Line Siting: Using ArcGIS ModelBuilder," *Advanced GIS Course Presentation, Idaho State University, Idaho Falls, ID, April 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Integrating Social Attitudes and Spatial Data in Siting Power Lines," *Oral presentation, 2011 International MapWindow GIS and DotSpatial Conference, San Diego, CA, June 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Integrating Social Attitudes and Spatial Data in Siting Power Lines," *2011 Western Energy Policy Research Conference, Boise, ID, August 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Integrating Social Attitudes and Spatial Data in Siting Power Lines Using the DotSpatial Framework: Introducing the LineSiter Application," *Poster Presentation, Free and Open Source Software for Geospatial (FOSS4G) Conference, Denver, CO, September 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Integrating Social Attitudes and GIS The LineSiter Application," *Engineering Seminar, Idaho State University, Idaho Falls, ID, November 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Integrating Social Attitudes and GIS The LineSiter Application," *World GIS Day, Idaho State University, Pocatello, ID, November 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, and J. Carlisle, "Stream Flow and Least Cost Path Analysis: An Algorithmic Comparison," *Idaho Statewide Water Seminar, Idaho State University, Idaho Falls, ID, November 2011.*

Beazer, R., D. Ames, J. Joe, D. Solan, D. Koehler, J. Carlisle, and R. Katnal, "Integrating Social Attitudes and Spatial Data in Siting Power Lines Using the DotSpatial Framework: Introducing the LineSiter Application," *Idaho State Board of Education, Idaho Falls, ID, June 2012.*

Beazer, R. and D. Ames, "Integrating Social Attitudes and Spatial Data in Siting Power Lines Using the DotSpatial Framework: Introducing the LineSiter Application," *Free and Open Source Software for Geospatial Conference, Denver, Colorado, September 2011.*

Beazer, R., D. Ames, D. Solan, J. Carlisle, and J. Joe, "Integrating Social Attitudes and Spatial Data in Siting Power Lines," *2011 Western Energy Policy Research Conference, Boise, Idaho, August 2011.*

Carlisle, J., J. Joe, D. Solan, D. Ames, and R. Beazer, "Public Reactions to Energy Transmission Siting: The Role of Nimbyism," *Annual Meeting of the American Political Science Association, Seattle, Washington, September 2011.*

Carlisle, J., J. Joe, D. Solan, D. Ames, and R. Beazer, "Energy Transmission Siting: The Social Bases of Support," *2011 Western Energy Policy Research Conference, Boise, Idaho, August 2011.*

Joe, J. and S. Piet, "Better Public Engagement and Management of Technical Challenges: Keys to Addressing Wicked Energy Policy Problems," *2011 Western Energy Policy Research Conference, Boise, Idaho, August 2011.*

Solan, D., "Transmission Siting Decision Support Tool: Integrating GIS and Social Risk," *Pacific Northwest Economic Region 21st Annual Summit, Portland, Oregon, July 2011.* (invited)

Solan, D., "Transmission Siting and Options for Improvement: Incorporating GIS Tools and Social Risk," *Northwest Wind and Wildlife Workshop, Portland, Oregon, June 2011.* (invited)

Solan, D., "Transmission Siting Decision Support Tool," *National Wind Coordinating Collaborative, Quarterly Meeting, Boise, Idaho, November 2010.* (invited)

Design and Operational Improvements, and LCA in Anaerobic Digestion of Fermented Dairy Manure Using a Two-Stage Process

Erin Searcy, Aurelio Briones,[1] Erik Coats,[1] Armondo McDonald,[1] Dennis Keiser,[1] Dev Shrestha,[1] Kevin Feris,[2] and Timothy Magnuson[3]
10-080

Current dairy manure management strategies such as anaerobic digestion (AD) or lagoon storage/land application don't fully recover valuable organic matter and are ineffective in handling greenhouse gas (GHG) emissions or removing nutrients. While AD is a mature technology that handles multiple substrates, cost and operational challenges have minimized use. Common operational challenges are variable pH and ammonia inhibition of organisms. Conventional two-stage AD involves manure fermentation in a tank followed by AD of the supernatant in another tank. This operational configuration may address the pH issue, however valuable organic matter remains unrecovered, and ammonia inhibition is not necessarily remedied. If we conversely focus on maximizing resource recovery from the manure, we could simultaneously produce multiple high value commodities while addressing environmental concerns. This project will focus on the production of two high value commodities, CH_4 and biofuels, and treatment of nutrients in the AD effluent.

Our objective was to design and study two novel processes for maximizing recovery and conversion of Idaho dairy manure into energy products. The first process maximized conversion of pre-fermented manure to methane (CH_4), while the second sequestered AD emissions (CO_2, nitrogen [N], phosphorus [P]) to produce lipid-rich algae that can be recovered and converted to biofuels. A life cycle analysis (LCA) characterized the system. A two-stage fermentation and AD test apparatus was assembled to test system impact on CH_4 production from manure. The supernatant was separated from the solids, and the effectiveness of nutrient removal using encapsulated algae (which may limit shear stress and increase lipid production) was studied and compared to lipid and biomass production by unencapsulated algal cultures.

Summary

This project focused on advancing an integrated suite of technologies that collectively maximize resource recovery for bio-energy production from animal manure (in this case, dairy manure was the focus).

Two-stage AD process description—Initial research into this novel two-stage AD process focused on validating the potential to actually achieve anaerobic digestion and methane production on manure that had been fermented (i.e., most of the readily degradable carbohydrates hydrolyzed and fermented to VFAs) and that was without most of the VFA-rich liquid fraction diverted to another biological process. Over an 85-day operational period the average biogas production for AD1 and AD2 was statistically identical, averaging 54.5±9.1 and 51.8±7.9 L/d, respectively. Similarly, the biogas methane contents were nearly identical at 51.4% and 54.3%, respectively; the methane content was typical of manure ADs. Of note, AD1 was organically loaded at a slightly higher rate than AD2; even further, volatile solids destruction in AD1 (43.7%) was slightly higher than AD2 (40.6%). While the latter outcome was expected given the partially pre-oxidized state of manure fed to AD2, collectively these results suggest that the microbial consortium in AD2 was more metabolically robust in order to produce the comparable biogas and methane quantities from lower quality and less organic matter. Regarding the microbial population, molecular analysis of archaea in the ADs revealed that both systems were highly enriched with *Methanosarcinaceae* (Msc), which are acetoclastic methanogens. However, AD2 exhibited a much larger fraction of Msc (estimated 70-99%) as contrasted with AD1 (12-48%), validating in fact that our two-stage AD enriched for a much more robust population of methane producers.

[1] University of Idaho

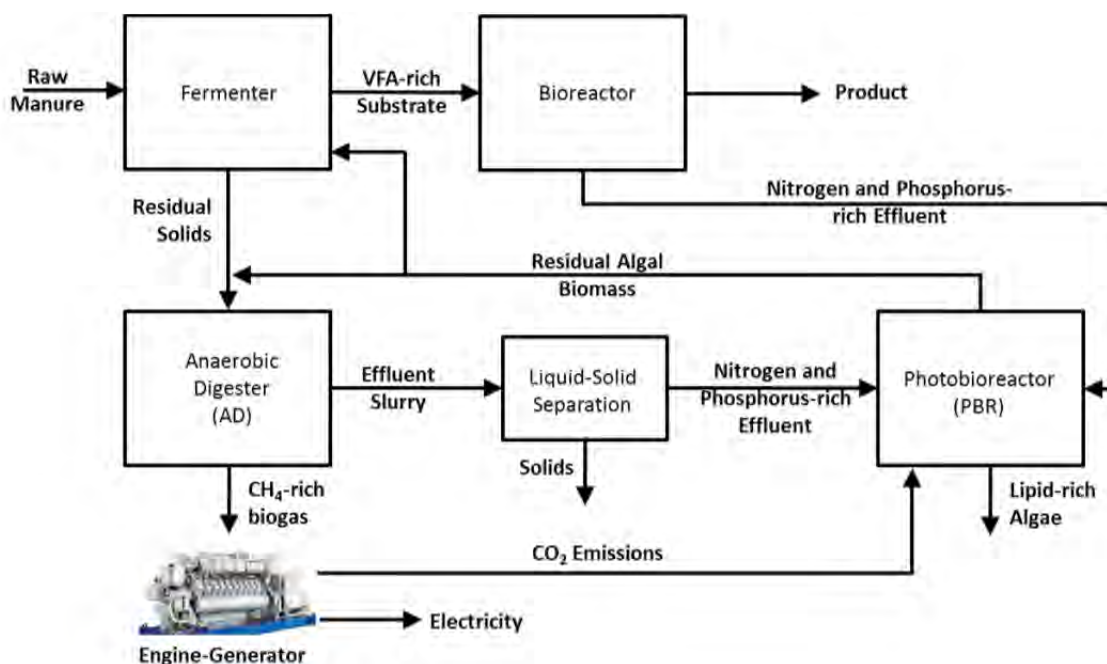[2] Boise State University

[3] Idaho State University

FIGURE 1. Proposed dairy manure to biofuel/bioower/bioproducts process. The two-stage anaerobic digestion process integrates processes to maximize recovery and conversion of valuable manure constituents to multiple high value commodities.

Having demonstrated the feasibility of our two-stage AD configuration, two new AD operations were evaluated to further characterize process potential. AD3 and AD4 were operated at 20 and 30 d SRTs/HRTs (with both ADs coupled to a fermenter, again operated at a 4 d SRT/HRT). Of note, while the organic loading rate (OLR) decreased slightly in AD3 and AD4 as compared with AD2, biogas production normalized to gVS destroyed was similar or higher. Over a 334-day operational period the average biogas production for AD3 and AD4 averaged 40.8±6.9 (55.8% CH_4) and 42.7±6.8 L/d (54.4% CH_4), respectively. The reduced biogas production was a consequence of receiving lower quantities of organic matter. Similar to that observed in AD1 and AD2, biogas production over an operational cycle was relatively consistent.

Microbial Ecology—Overall, the microbial ecology of two-stage AD appears to reflect a diverse and robust microbial community. Sequencing analysis of samples collected from AD1 to AD4 as well as field samples from a full-scale dairy manure AD are ongoing. The power of next generation sequencing efforts will be best realized when we correlate sequencing data to experimental perturbations imposed to test robustness or stability; and when we identify the core constituents or the 'core microbiome' associated with dairy manure AD. The latter will require analysis of various 'real world' AD systems, the rationale and procedures of which can be modeled after similar efforts currently being undertaken to study the human microbiome.

Proteogenomic analysis of anaerobic digestor effluents— We were able to identify Streptomyces alpha-mannosidase and a 1,2-homogentisate hydroxylase, two enzymes involved in sugar metabolism and aromatic compound (lignin) breakdown, respectively.

Algae Production—The ammonia present in the AD effluent reduced algal yield and increased the lag time to reach the log phase of growth, resulting in 78% less chlorophyll and 35% less biomass after a 2-week incubation. Acetate was found to be inhibitory, resulting in a 34% decrease in chlorophyll and biomass yield. The final chlorophyll concentrations for sodium propionate and NaCl flasks were 7.59(2.40) mg/L and 11.54(8.54) mg/L. Although the NaCl flasks in this experiment were visibly different than the

sodium propionate, the high standard deviation for the chlorophyll measurements resulted in no statistical difference between the two treatments.

Nutrient sequestration—<u>Nitrogen</u>: When grown on AD effluent there was an initial increase in total dissolved nitrogen, with an overall 21-day reduction for the Chlorella vulgaris and an environmental strain of Chlorella isolated from a local municipal wastewater effluent pond, of 18% and 81%, respectively.

<u>Phosphorus</u>: The total dissolved phosphorus (TDP) was also measured using a persulfate acid digestion method and 0.45 μm filtered samples. Although TDP did change throughout the incubation period, similar to the nitrogen, there was no appreciable difference after the 21-day incubation period. This may be due to the residual particulate organic matter in the AD effluent that acts as a source of phosphorus and other nutrients that appears to be in flux with the solution throughout the 21-day period.

A novel strategy for pretreatment of the AD reactor effluent to limit photoinhibition of algal production: Ultraviolet (UV) Treatment—UV pre-treatment decreased the length of the lag phase by an average of 10 days, even after just 30 seconds of UV treatment. This decrease in the lag phase is potentially achieved by either reducing the number of prokaryotic competitors in solution or by modifying the quality of the DOM thereby reducing the potential for photoinhibition. However, UV treatment does not increase the available dissolved phosphorus and therefore the net yield does not increase relative to the controls, although the time to achieve stationary phase growth is dramatically reduced.

Lipid production—The lipids from *B. bruani* are mainly (90%) triterpenes ($C_{34}H_{58} + C_{32}H_{54}$) as determined by GC-MS analysis with a minor amount of triglycerides (10%). The Chlorella strains contained only triglycerides. The triglycerides were characterized as their fatty acid methyl ester derivatives and were mainly C16 and C18 fatty acids.

Impact on GHG Emissions—The performance of the anaerobic digester varied depending on the time of the year. All of the anaerobic digesters experienced some problems and had to close for at least part of the year. AD1 had 12% downtime and, AD2 had 15% down time and AD3 had 14% down time. The primary cause of this down time was the issue of solid retention and crusting within the

digester. Crusting caused the digester to be shut down for several days.

The GHG emissions from the base case waste management system that uses only anaerobic lagoons were compared with the GHG emissions with anaerobic digesters. On average, the anaerobic digesters reduced the GHG emissions by 42%. In addition to the existing anaerobic digester, a GHG emission impact from the improved two stage digester was also studied. The pilot scale single stage anaerobic digester performed similar to the real AD in terms of amount of methane produced per unit of volatile solids handled by AD. This provided a basis for comparing laboratory results with real-world digester results. When a two-stage anaerobic digester was up-scaled to replace existing digesters, the additional reduction in GHG emission was significant. The main advantage of the two-stage AD was coming from overall higher volatile solids destruction rate that helped reduce the methane from downstream of AD.

The project developed partnerships with local universities, which not only expands DOE's capabilities but also introduces potential future researchers to DOE work. Several students have been supported to various degrees through this project.

The project continues to build collaborations through proposals, which can lead to future funding. Several proposals have been funded through this project, including:

- Enhancing Greenhouse Gas Mitigation and Economic Viability of Anaerobic Digestion Systems: Algal Carbon Sequestration and Bioplastics Production. Funding Source: Agriculture and Food Research Initiative.

- Integrated Approach to Algal Biofuel, Bio-power, and Agricultural Waste Management. Funding Source: INL LDRD (CAES).

- Biological Pretreatment of Agricultural Waste with Biochar Amendment Prior to Solid-state Anaerobic Digestion. Funding Source: UI Seed Grant Program.

- Developing Strategies to Increase Prosperity for Small Farms through Sustainable Livestock Production, Processing and Marketing. Funding Source: U.S. Department of Agriculture (USDA).

- Lifecycle Analysis of Pacific Northwest Feedstocks for Biofuel Production. Funding Source: Environemental Protection Agency (EPA).

- Energy and Environmental Life-cycle Analysis of Camelina Biofuel. Funding Source: USDA.

- CAES Energy Efficiency Research Institute Industrial Assessment Center for the Inland Northwest. Funding Source: DOE.

- MRI: Acquisition of an Ion Torrent PGM Sequencer for Research and Education. Funding Source: National Science Foundation (NSF).

- Conversion of Agricultural Wastes to Biofuels. Funding Source: T.S. VerdureTech, Inc.

- Synthesizing Polyhydroxyalkanoates from Fermented Dairy Manure. Funding Agency: NSF Environmental Sustainability Program.

- Pilot-scale PHA Production on Fermented Dairy Manure. Funding Source: Idaho Dairymen.

- Biological Recycling of Algal Water and Nutrients (BRAWN). Funding Source: DOE Advancements in Sustainable Algal Production program.

- PPCPs in Biosolids – Fate and Treatment. Funding Source: Northwest Biosolids Management Association.

Benefits to DOE

This project has benefited DOE national security missions by helping develop safe, competitive, and sustainable energy systems using U.S. resources.

Relevant Publications and Presentations

Coats, E., I. Ibrahim, A. Briones, and C. Brinkman, "Methane Production on Thickened, Pre-Fermented Manure," *Bioresource Technology*, Vol. 107, 205-212, 2012.

Artrip K. and D. Shrestha, "Life Cycle Analysis of Various Dairy Manure Anaerobic Digestion Systems*," ASABE International Conference Presentation, ASABE Paper # 121337099, Dallas, Texas, 2012.*

Ellis, J. and T. Magnuson, "Thermostable and Alkalistable Xylanases Produced by the Thermophilic Bacterium Anoxybacillus Flavithermus TWXYL3," ISRN Microbiology, 2012. (in press)

Artrip, K., D. Shrestha, E. Coates, and D. Keiser, "GHG Emissions Reduction from an Anaerobic Digester in a Dairy Farm: Theory and Practice," *Applied Engineering in Agriculture*, 2011. (in review)

Coats, E., "Toward Implementing an Integrated Set of Processes for Upcycling Dairy Manure and Minimizing Environmental Emissions," *Pacific NW Animal Nutrition Conference, Portland, OR, October 2011.* (invited)

Artrip, K., D. Shrestha, and D. Keiser, "Reducing Greenhouse Gas Emissions on Idaho Dairy Farms Through the Use of Anaerobic Digestion Systems," *Bioenergy Research Collaboration Symposium, University of Idaho, Moscow, ID, 2011.*

Artrip, K. and D. Shrestha, "Life Cycle Analysis of Various Dairy Manure Anaerobic Digestion Systems," *ASABE International Conference, Dallas, TX, 2012.*

Coats, E., "Toward an Integrated Set of Processes for Enhanced Economic Valuation of Dairy Manure – Looking Beyond Anaerobic Digestion," *2nd Annual Idaho Research Symposium, Boise, ID, February 2, 2012.* (invited)

CAES Vertical Axis Wind Turbine

Kurt Myers, John Gardner,[1] and Damon Woods[1]
10-088

Wind and hydro turbines that use articulated foils for energy capture have interesting potential but have not been investigated in totality. To better evaluate these innovative designs, we developed analysis and modeling tools. In particular, our tools address turbines that incorporate energy capture elements (wings or foils) that are largely parallel to the axis of rotation and designs in which these elements articulate throughout the revolution of the turbine. In addition, the utility of these new tools to inform the design optimization process also is being assessed.

The project originally developed tools for a specific Vertical Axis Wind Turbine (VAWT) design proposed by a Boise, Idaho company. A prototype turbine was made available for INL and Boise State University (BSU) researchers for a time; however, detailed field validation tests were limited since the turbine was recalled partway through the process.

The physics of wind turbines and hydro turbines with articulating blades is very similar and the basic tool framework applies equally well to both domains. The tools incorporate the following features: solid body dynamics of the turbine rotor, simplified generator model to provide load, kinematic model to enforce foil articulation as a function of rotor rotation, computation of the net velocity seen at the foil as a function of the fluid velocity and the relative motion of the foil, computation of the instantaneous angle of attack, look-up tables for the lift and drag coefficients, and computation of the instantaneous net torque provided by the foils as the driver for the rigid body dynamics. In addition, we incorporated a model for the "induction factor" (a measure of reduction in fluid velocity due to energy extraction by the turbine) into the models. For hydro turbine models, the induction factor computation also includes water depth in channel up and downstream of the turbine.

This project has also significantly added to the historical work and effective team building between INL and BSU (national laboratory/university collaboration). The BSU and the INL wind program have worked together for many years on regional wind development activities and student development in the area of renewable energy. The collaboration has led to significant contribution to the workforce pipeline, both for DOE and private industry. This particular project has resulted in a Master's degree student entering the workforce.

Summary

This project developed detailed, physics-based computer simulation models of articulated foil wind and hydro-turbines. Figure 1 shows the fundamental outline of the models schematically.

Two versions of the model were developed in Matlab/Simulink. One version modeled a vertical axis wind turbine, and one modeled a "run-of-river" hydroturbine design in which the axis of rotation is transverse to the channel.

The VAWT model is well-validated against published performance data. In addition, we used the model to discover potentially valuable features of VAWT behavior. Specifically, we found that the VAWT with articulated foils was capable of significantly better performance if allowed to operate in higher speed ranges, where the tip speed ration (TSR) was on the order of 4 or 6. This runs counter to the conventional wisdom that suggests TSRs in the neighborhood of 1 are optimal. Further investigation of this phenomenon indicates that other researchers have observed this behavior. Figure 2 shows a typical simulation output demonstrating this behavior.
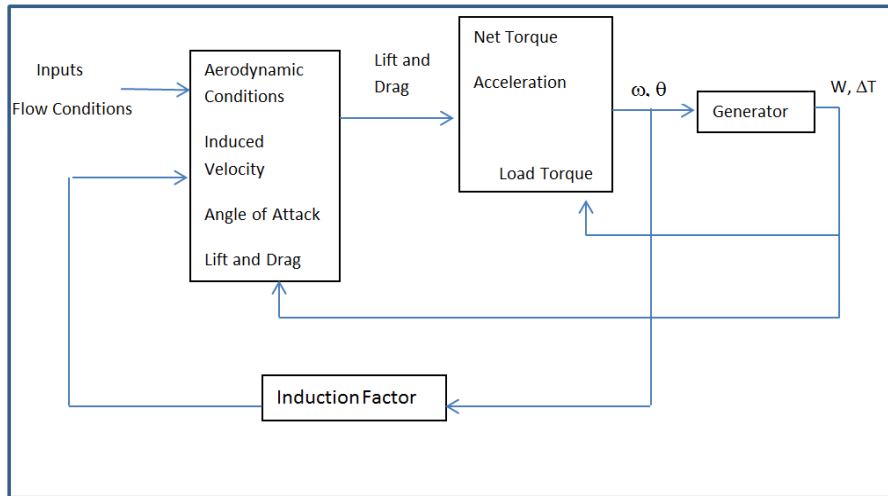
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[1] Boise State University

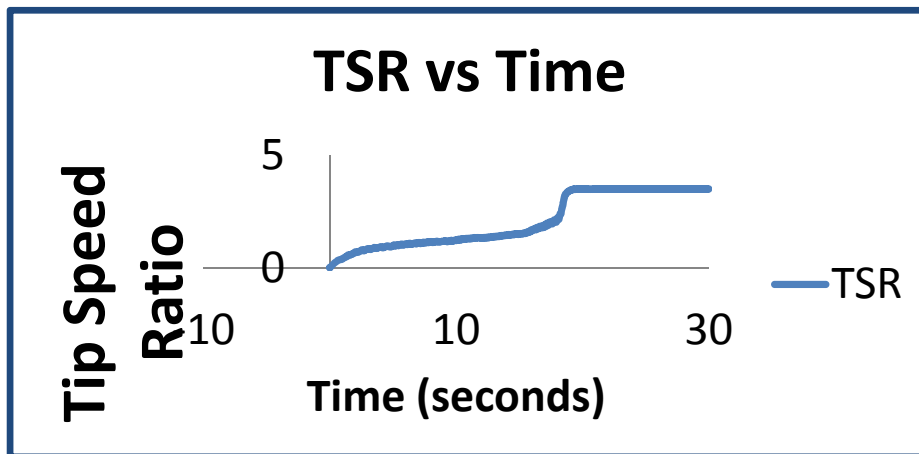**FIGURE 1**. Schematic of the turbine dynamic model.

FIGURE 2. VAWT performance showing a transition to high-TSR domain.

Benefits to DOE

This project developed analysis and design optimization tools for a class of wind and hydro turbines that have previously received little attention from the research community. A few examples of commercial prototypes using articulated foils are available, but the complexity that they present make the need for such tools apparent. Leveraging the scientific eminence at the INL, the analysis tools developed from this project will be useful for future design, development, and deployment of such turbines, and will enhance the energy security and energy sustainability missions of the DOE.

Relevant Publications and Presentations

Gardner, J. and D. Woods, "Dynamic Modeling of an Articulating Rotor VAWT," *AWEA Windpower 2011 Conference, Anaheim, CA, May 22-25, 2011.*

Woods, D., "Predicting Turbine Performance with a Dynamic Computer Model," M.S. Thesis, Boise State University, December 2012.

Development and Demonstration for National Fuel Efficiency

David Gertman, Milos Manic,[1] and David Bruemmer[2]
11-065

According to the U.S. Energy Information Administration, the U.S. transportation sector (including cars, trucks, buses, and tractor-trailers) consumes more than two hundred billion gallons of fossil fuel each year. There are over 2.5 million heavy trucks on the highways and while medium and heavy trucks represent only 4% of all vehicles, they collectively use more than 20% of all fuel. One category of heavy trucks—long-haul heavy duty tractor trailers—use over 22 billion gallons of fuel annually. These vehicles are critical to our economy and transport goods hundreds of millions of miles back and forth across the country each year. Even a small increase in fuel efficiency for these vehicles results in tremendous cost savings as well as reductions in emissions.

It is widely recognized that improvements in human behavior can significantly improve fuel efficiency. A 2004 study by truck maker International found that improvements in driver behaviors could yield significant (20-30%) improvements in fuel efficiency between drivers without changes in the vehicle hardware or software. Other studies have similar findings. Rapid acceleration, improper speed selection for conditions, unnecessary braking, excessive idling, and poor route selection, are among the human factors that are recognized to reduce fuel economy. In Phase I of this LDRD project, we focused on evaluating improper speed selection and acceleration characteristics under varying slope conditions, i.e., changes in elevation, for a fixed route from the INL site to Idaho Falls. Of resources that can be optimized by fleet operators, none is more valuable (or variable) than the human operator. Consequently, implementation of an inexpensive system that helps drivers reduce petroleum use behaviorally can save fleet operators many millions of dollars with the byproduct of environmental and national security benefits.

This project is being conducted step-wise in three phases over three years. The first phase focused on development of a successful software architecture including algorithm development and real time data management leading to an initial functional prototype system. Phase 2 focused on hardware development, implementation, and product solution including development of a driver interface that will promote driver efficiency awareness without degrading situation assessment. A prototype of that interface is now complete. Phase 3 efforts are maturing these capabilities through field testing using motor coaches and bus drivers from the current INL fleet.

Summary

During the course of this project, through the collaboration of the University of Idaho (UI) and INL, we have built a highly effective team that is using advances in technology (sensors) and computer sciences (neural networks) to improve INL site driver and motor coach fleet efficiency. Ultimately, these improvements will be applicable to the DOE complex and will support commercial fleet efficiency. One of the major byproducts beyond building the core competency within the DOE and the University has been the contribution to the future DOE workforce that we are making through the support of graduate students. During the course of this collaborative effort, four different graduate doctoral level students from UI were supported. Additionally, our presentations at the 2012 National FedFleet Conference in Louisville, recognition and interest from MCI Motor coach (the largest vendor for GSA-purchased motor coaches), and a recent presentation at the Institute of Electrical and Electronics Engineers (IEEE) conference on Human System Interaction in Perth Australia, 2012, have contributed toward CAES, University, and INL scientific eminence.

The first two phases of this project focused on establishing an initial parameter set needed to optimize bus fuel efficiency across a variety of drivers. Progress was made on: data mining in support of building the initial model; identifying a software architecture to support communications, data capture, and data reduction strategies. In parallel to this work, a simulation has been developed to gage driver response to efficiency prompting, and to train them to an interface that would establish efficiency awareness. Formal training to the system is planned for Phase 3. The initial simulation, VBUS, was developed by UI and is being used to refine our underlying model as well as to collect information on interface design.

A sample of some of the data logging from our simulation work is presented below in Figure 1.

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[1] University of Idaho

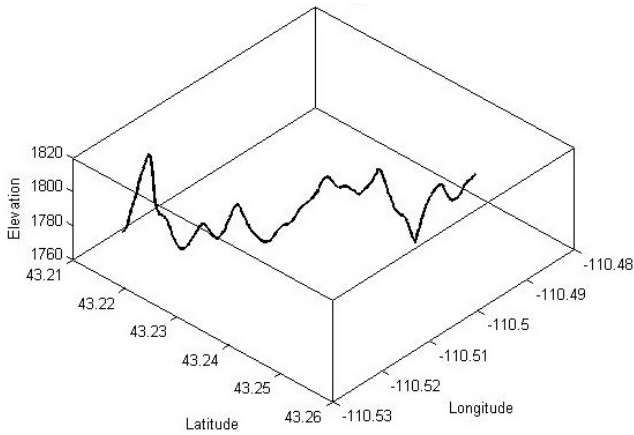[2] 5D Robotics, Carlsbad, New Mexico

FIGURE 1. Data logging as a function of elevation.

These data are representative of the type of changes in elevation associated with certain route characteristics around the INL site. Gas pedal displacement, another variable constituting part of the model is presented in Figure 2. The pedal displacement and fuel rate usage have been sampled from a test using an INL motor coach. When field experiments are conducted in FY 2013, pedal position, elevation, and efficiency data will be compared for prompting and non-prompting conditions.
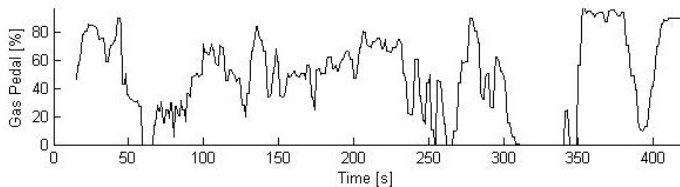
FIGURE 2. Gas pedal displacement.

To date there has been considerable innovation in the following areas:

• Model and driver efficiency algorithm development

• Simulation capability

• Real time collection capability (information on over 200 parametric variables can be acquired and compared) using the NEXIQ technologies USB link system

• Refinement of a set of key parameters for model building and real time information synthesis for drivers

• Development of a prototype graphic user interface

• Architecture allowing for collection and data management for large amounts of real time sensor data.

Benefits to DOE

This project is seeking to reduce fuel usage among an important portion of the country's transportation industry. Such a reduction supports DOE's mission of energy security by saving transportation fuel. Reduced fuel usage also reduces CO_2 emissions while potentially saving millions of dollars. The benefits of this project would be felt throughout the nation.

Relevant Publications and Presentations

Linda, O. and M. Manic, "Improving Vehicle Fleet Fuel Economy via Learning Fuel Efficient Driving Behavior, in Proceedings," *2012 IEEE International Conference on Human System Interaction, IEEE, Perth, Australia, June 6-8, 2012*.

Targeted Energy Management Toolset for Comfort and Savings Based on Advanced Computational Intelligence Techniques

Craig Rieger, Milos Manic,[1] Kevin Van Den Wymelenberg,[1] and John Gardner[2]
11-066

Preliminary work suggests that changes in energy management could easily lead to cost reductions above 10%. In addition to optimizing existing Energy Management Systems (EMS), this project is working on a toolset that will be both resilient and secure in order to proactively maintain a safe level of operational normalcy in response to anomalies and malicious actions. The primary objective of this work is the development of a toolset that integrates advanced sensor systems with advanced computational intelligence (e.g., neural networks and fuzzy arithmetic) to enable effective energy management while minimizing negative human comfort consequences and promoting improved occupant satisfaction. The main technical advantage of this work is the development of a "bolt-on" toolset that brings advanced computational power to existing EMS in a secure and resilient manner. Novel features include the integration and modeling of human comfort/occupancy and energy usage data to enable building managers to achieve both energy efficiency and optimal human comfort. The project's tasks are:

- Select representative buildings for evaluation of potential use in the final demonstration

- Create an initial version of the analysis and visualization tool based on the input from the surveyed building managers

- Install supplemental sensors and control devices to further demonstrate the benefits of new technology, as integrated with the toolset

- Develop human comfort surveys to allow individual feedback on areas of concern within the building environment

- Review the functionality that will be performed with the chosen scenario building managers.

Summary

Three buildings were selected for evaluation on this project: Banner Bank and the Mobilization and Training Equipment Site (MATES) facilities (both in Boise, ID) and the Center for Advanced Energy Studies building (in Idaho Falls, ID). In addition, INL's UB4 facility will be used for additional testing and evaluation. Within these facilities, individual types of occupancies have been selected and EMS data has been provided by the building managers for evaluation. Supplemental wireless systems will be installed and remotely transmit CO_2, radiant temperature, air temperature, occupancy, and ambient light. A survey was also created for the building occupants to provide the primary mechanism of correlating human comfort within occupied spaces.

In addition, a scalable Bluetooth sensor pack that includes temperature, humidity, and ambient light has also been created (see Figure 1). This system can be coupled with a human comfort feedback application (see Figure 2), developed for an Android-based smart phone, to record individual perceptions against baseline data (University of Idaho [UI]).
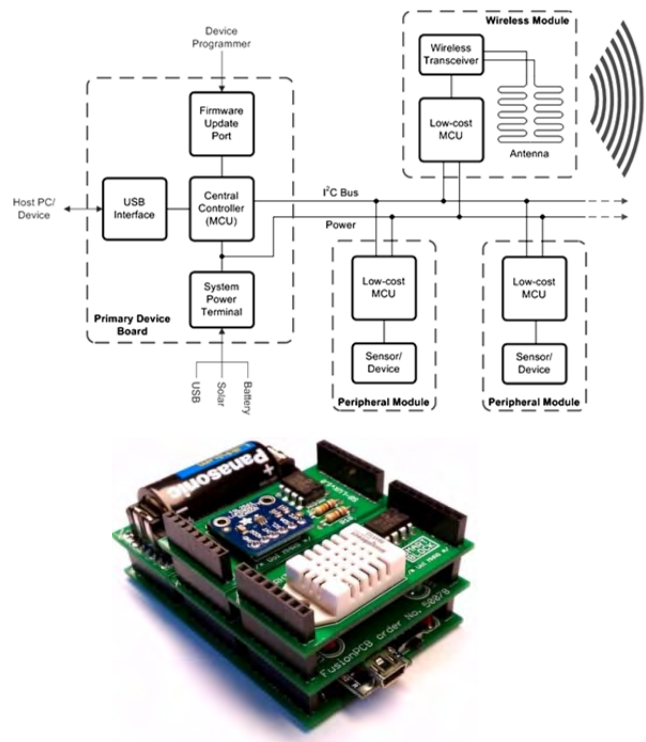
FIGURE 1. Scalable Bluetooth Sensor Design (top) and Sensor Prototype (bottom).

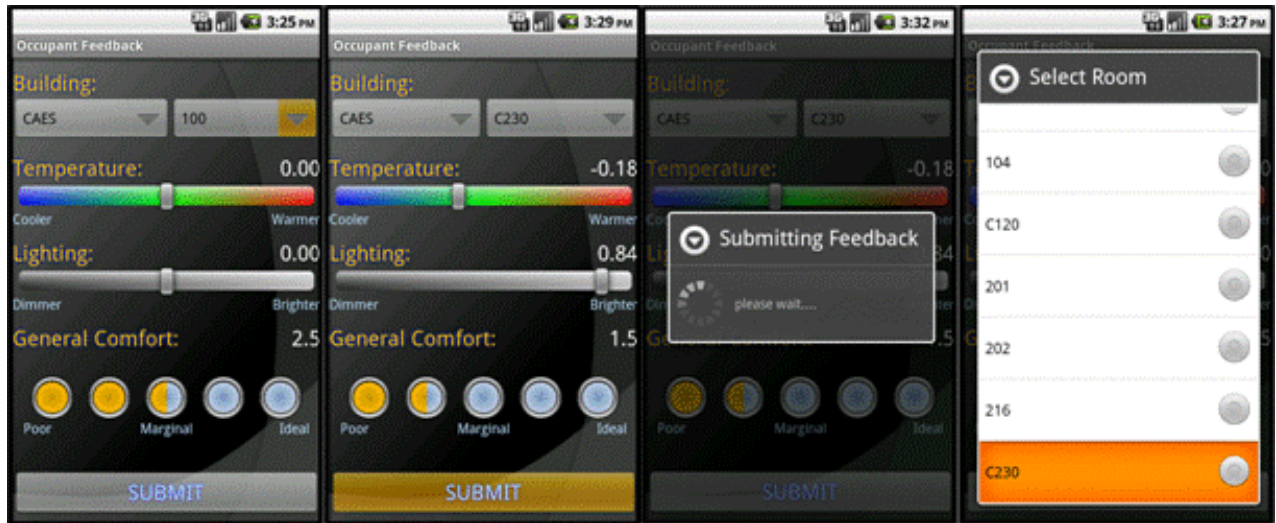[1] University of Idaho

[2] Boise State University

FIGURE 2. Human Comfort Feedback Application. (UI)

The initial design of the analysis and visualization tool has been developed based upon Banner Bank and MATES EMS data (see Figure 3). The display provides spatial and temporal representation of individual physical parameters, and allows individual thresholds to be established to characterize normal behaviors and flag anomalies. The implementation includes a fuzzy logic design that allows pre-established, as well as building manager designed rule sets to tailor the desired anomalies and patterns in the building for single or multiple physical parameters. A separate evaluation to show connectivity between individual physical parameters within the data was also performed using self-organizing maps, which could be integrated within the analysis and visualization tool as desired. One demonstration of the tool has been already performed, with another planned for building managers before the end of the year.

Benefits to DOE

A key barrier to the widespread adoption of existing energy efficiency technologies is the low return on investment realized by users. The proposed technical advance will contribute to DOE's efforts to reduce dependence on energy imports through energy efficiency by enabling the more effective use of existing EMS via a bolt-on toolkit. An actionable information tool will be provided for building managers through an innovative and multidisciplinary approach that integrates human comfort

principles with advanced real-time visualization and control tools.
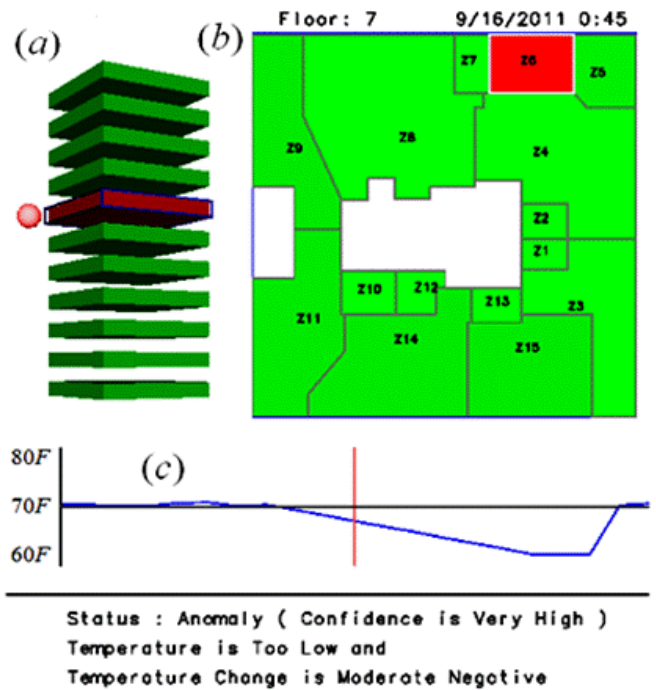

FIGURE 3. Analysis and Visualization Tool: (a) building, (b) floor, and (c) data.

Disciplinary perspectives were brought in from a diverse set of University of Idaho, Boise State University, and Idaho National Laboratory researchers in mechanical engineering, architecture, computer science and electrical engineering and human factors. The team benefited from individual research in resilient controls and energy efficiency to apply toward a holistic, human-enabled approach to intuitive design of energy efficiency tools. Several graduate students and a postdoc have been participating in the development of the toolset, mentoring a new generation of individuals that recognize the value of multidisciplinary involvement in addressing multifaceted issues such as energy efficiency.

Relevant Publications and Presentations

McCarthy, K. and M. Manic, "A Proposed Data Fusion Architecture for Micro-Zone Analysis and Data Mining," *IEEE ISRCS 2012, Salt Lake City, UT, August 2012*.

Hewlett, J., M. Manic, and C. Rieger, "WESBES: A Wireless Embedded Sensor for Improving Human Comfort Metrics Using Temporospatially Correlated Data," *IEEE ISRCS, Salt Lake City, UT, August 2012*.

Ondrej, L., D. Wijayasekara, M. Manic, and C. Rieger, "Computational Intelligence Based Anomaly Detection for Building Energy Management Systems*," IEEE ISRCS, Salt Lake City, UT, August 2012*.

Rieger, C., "Energy Security and Resilient Control Systems," *Idaho National Laboratory and the University of Southern California's Information Sciences Institute, November 15–16, 2011*.

Duarte, C., B. Acker, R. Grosshans, M. Manic, K. Van Den Wymelenberg, and C. Rieger, "Prioritizing and Visualizing Energy Management and Control System Data to Provide Actionable Information for Building Operators," *Western Energy Policy Research Conference, Boise, ID, August 25–26, 2012*.

Alert/Alarm Dashboard

Ronald Boring, David Gertman, and Brian Dyre[1]
12-086

Advances in theoretical and applied knowledge with regard to alarm systems at nuclear power plants (NPPs) are needed. The focus of this research is to develop first principles of alarm management that will help establish the technical basis for the design of new alarm systems at NPPs. This project covers two steps toward improved alarm systems.

Step 1. Evaluation of alarm management system technologies. INL and the University of Idaho (UI) have reviewed various alarm management system principles and technologies and are working to deploy them on a simulator. In addition, the research team has developed a plan for testing operator performance with these systems.

Step 2. Deployment of a microworld simulator model for nuclear power plant process control. A microworld simulator represents a simplified form of the process control system that may be tailored to less skilled operators. While full-scale high-fidelity control room simulators exist for research on displays and control systems and training of operators, their utility is limited by high demands on technical staff and expensive facilities that greatly increase overhead costs. Research with such simulators also requires a pool of trained operators— whose time is very constrained—to act as research participants. These factors are significant barriers to conducting efficient empirical research on novel display and control systems or providing training that does not necessitate full-scale, high-fidelity simulation. For research, more efficient use of limited resources could be realized by using lower-fidelity "microworld" simulations that would allow DOE researchers and their collaborators to focus on particular display and control issues (e.g., decision making and prioritization of actions in response to alarms) using a low-cost simulation that mimics the perceptual, cognitive, and action processes of real-world process control in a more tightly-constrained microworld environment. An additional advantage of the microworld environments is that ideas for novel displays and controls can be examined in a simplified context that does not necessarily require trained operators to act as participants. Novel display and control concepts can be tested quickly and efficiently using the microworld, and those concepts that show promise can then be further tested using full-scale, high-fidelity simulation with trained operators. In addition, the flexibility

of the microworld can provide trainees a view of the internal dynamics of a process control system much more efficiently than using a full-scale high-fidelity control-room simulation.

Summary

Alarm Technologies. Decision support such as alarms for operators is not new, and much has been written regarding the potential usefulness of digital support systems and alarm filtering strategies. However, determining the appropriate characteristics of decision support tools is difficult, especially when alarms can vary in the manner which diagnostic information is formulated and displayed and when event scenario types are complex and numerous. When first reviewed, the advantages or disadvantages of a particular alarm approach may not be apparent to the designer or analyst.

Microworld Development. The research in FY 2012 centered on developing a flexible and scalable microworld simulation environment by UI and INL staff. UI was responsible for developing the code, while INL staff provided specifications and technical guidance on the implementation. The development approach is loosely based on previous microworld simulators used for research purposes, such as the University of Toronto's DURESS. The DURESS simulator presents operators (or research participants) with a simple process control task wherein the operator must control valves, pumps, and heaters to ensure a given output flow and temperature. System faults can be introduced that require the operators to engage in troubleshooting and fault diagnosis. DURESS was specifically designed to examine how ecological interface displays might aid in these processes with one particular task—controlling the flow rate and temperature of the output water flow. The joint INL-UI Microworld Simulator could be used similarly, but has been designed to be much more flexible and include components and processes that are of more direct interest to nuclear power control systems.

Two related software tools, a visual microworld scenario editor and a microworld scenario simulator (the player), have been developed for training and research using Oracle's platform-independent Java language. The editor provides a visual tool in which a variety of system components can be visually created and connected using a drag-and-drop visual interface. Figure 1 shows an example

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[1] University of Idaho

of a simple interconnected set of pumps, pipes, valves, and reservoirs designed in the microworld scenario editor.

Benefits to DOE

The energy sector currently uses control rooms to control generation, transmission, and distribution of power sources. Each control room features alarm systems. While the focus of this research is primarily on alarm systems in nuclear power plants, this project is developing a set of alarm research methods that can be used across energy sectors to produce more effective alarms. This research has the opportunity to establish a core competence within DOE in alarm research for energy applications. It provides a pipeline of competent student researchers from the university setting who can support such research needs in the future. While the INL maintains a full-scope reconfigurable simulator for human factors studies of operators, in practice, this facility has proven costly to set up for research. The present research develops and validates a process-equivalent simulator at UI that can be used at INL for first principles research. The availability of a process-equivalent microworld simulation significantly increases the frequency and variety of empirical human factors studies that the INL can complete.
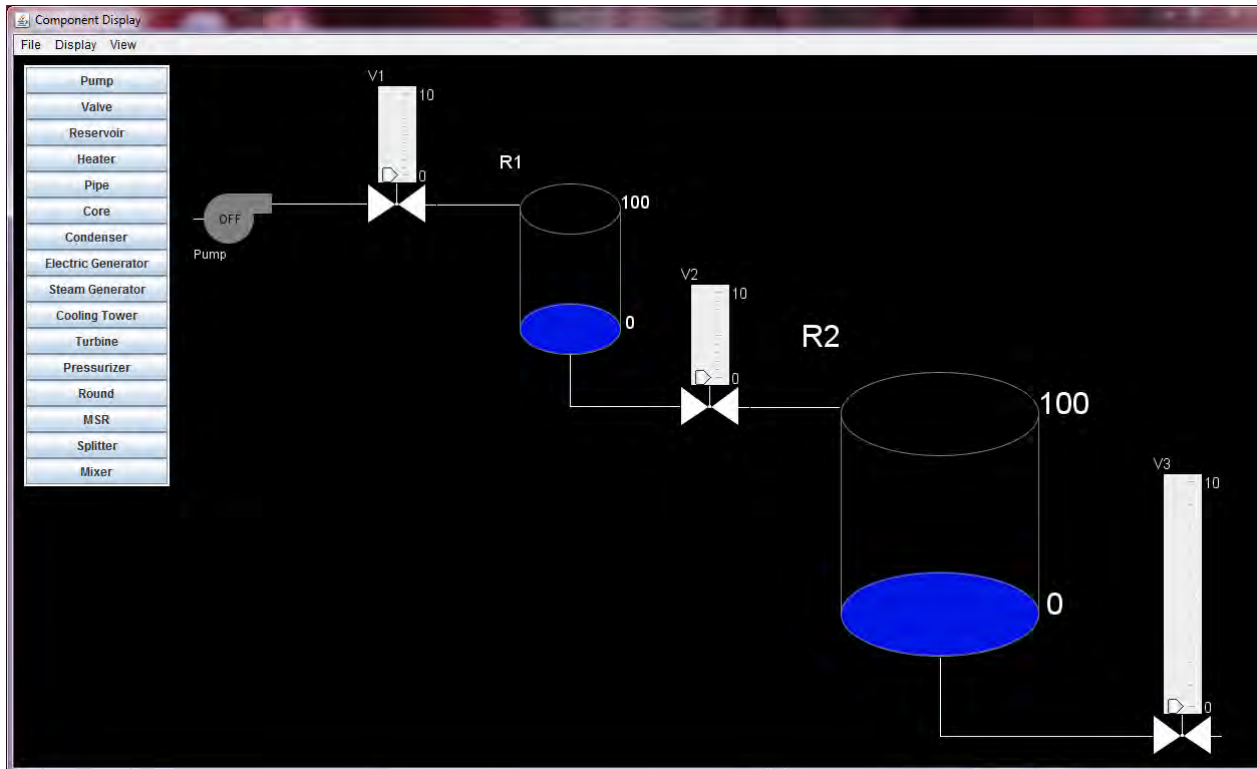

FIGURE 1. A simple process control microworld shown in the editor window.

Relevant Publications and Presentations

Boring, R.L., D. Kelly, C. Smidts, A. Mosleh, and B. Dyre, "Microworlds, Simulators, and Simulation: Framework for a Benchmark of Human Reliability Data Sources," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference*, 16B-Tu5-5, 2012.

Boring, R.L. and J.J. Persensky, "Hybrid Alarm Systems: Combining Spatial Alarms and Alarm Lists for Optimized Control Room Operation," *8th International Topical Meeting on Nuclear Power Plant Instrumentation, Control, and Human-Machine Interface Technologies (NPIC&HMIT),* 1914-1923, 2012.

Ragsdale, A., "*Nuclear Power Plant Operator Performance When Systems Vary in Alarm Type, Alarm Accuracy, and Information Type,*" Master of Science Thesis, Department of Psychology, University of Idaho, 2012.

Ragsdale, A., R. Lew, B.P. Dyre, and R.L. Boring, "Fault Diagnosis with Multi-State Alarms in a Nuclear Power Control Simulator," *Proceedings of the Human Factors and Ergonomics Society 56th Annual Meeting,* 2012. *(in press)*

Ragsdale, A., R. Lew, B.P. Dyre, R.L. Boring, and D. Gertman, "Alarm Strategy and Complexity: Predictions of Operators Response," *8th International Topical Meeting on Nuclear Power Plant Instrumentation, Control, and Human-Machine Interface Technologies (NPIC&HMIT),* 1924-1932, 2012.

Boring, R.L., D. Kelly, C. Smidts, A. Mosleh, and B.P. Dyre, "Microworlds, Simulators, and Simulation: Framework for a Benchmark of Human Reliability Data Sources," *Joint Probabilistic Safety Assessment and Management and European Safety and Reliability Conference, Helsinki, Finland, June 25-29, 2012*.

Boring, R.L. and J.J. Persensky, "Hybrid Alarm Systems: Combining Spatial Alarms and Alarm Lists for Optimized Control Room Operation," *8th International Topical Meeting on Nuclear Power Plant Instrumentation, Control, and Human-Machine Interface Technologies (NPIC&HMIT), San Diego, CA, July 22-26, 2012*.

Ragsdale, A., R. Lew, B.P. Dyre, R.L. Boring, and D. Gertman, "Alarm Strategy and Complexity: Predictions of Operators Response," *8th International Topical Meeting on Nuclear Power Plant Instrumentation, Control, and Human-Machine Interface Technologies (NPIC&HMIT), San Diego, CA, July 22-26, 2012*.

CENTER FOR
ADVANCED MODELING AND SIMULATION

Study of Preconditioning Techniques for Krylov Solvers Applied to Hybrid Neutron Transport Calculations

Cristian Rabiti and Jim More[1]

10-023

Even with significant improvements in computing power, the challenge of performing a high fidelity neutronics simulation of a full nuclear reactor seems unrealistic for several years. On the other hand, strong local heterogeneities arising from control rods, transmutation targets, and reflectors, pose challenges with respect to the simulation accuracy that can be optimally met with a combination of different transport discretization in a single calculation. If successful, this research will enable us to tailor computational levels of accuracy to the needs of high fidelity simulations. We will accomplish this by developing preconditioners for use in conjunction with Krylov methods to perform neutronics analyses using different angular discretizations (different level of accuracy) in different reactor regions. We refer to calculations in which multiple discretizations are used as hybrid calculations. Examples of different angular discretizations are the even-parity discrete-ordinates equations (even Sn), the spherical-harmonics equations (Pn), and the method of characteristics. Our plan for the first year was to demonstrate effective local and global preconditioners for a mixed discrete-ordinates/ diffusion model in 1-D and then later on to generalize it to higher order spherical harmonics (diffusion in fact, represents the lower order of the spherical harmonic approximation). Note that the diffusion corresponds to the lower level approximation of the spherical harmonics based angular discretization of the transport equation. It was in fact the goal of the subsequent years to generalize such scheme to higher order approximation rather than the diffusion. Our local preconditioners are based upon block-Jacobi iteration schemes that are commonly referred to as response matrix methods. Our initial global preconditioners are based upon an overall diffusion approximation on the whole reactor core.

Very little research has been done relating to preconditioned Krylov methods for hybrid calculations. To our knowledge, this is the first time an overall global iteration approach has been tested.

Summary

We first completed a preconditioning scheme for 1-D, two-region problems using the discrete ordinate angular discretization (Sn) in one region and the diffusion approximation in the other. We initially considered a very simple fixed-point iteration scheme by which a complete Sn solve was performed using the in-flow from the diffusion region, followed by a complete diffusion solve given the latest in-flow from the Sn region. To summarize, the high fidelity (Sn) and low fidelity (diffusion) regions were solved independently and an iterative process was used to converge the information exchanged at the interface.

This scheme can be very inefficient when the scattering ratio in one or both regions is high. Nonetheless, when wrapped in a Krylov solver, the Krylov iterations always converged in two iterations because only the interface diffusion scalar flux and the interface diffusion current were in the Krylov vector, yielding an effective 2 × 2 system. It is very important to recognize that the Krylov vector need not contain every unknown that is solved for. Rather it need only contain the minimum number of unknowns such that, given exact values for these unknowns, the complete solution can be obtained with a single fixed-point iteration.

Our second fixed-point iterative scheme consisted of a Sn sweep in the transport region followed by a global diffusion solve. In the transport region, the diffusion solution provided an additive correction to the Sn iterate for the scalar flux and thus played the role of diffusion-synthetic acceleration in that region. In the diffusion region, the diffusion solution did not provide any sort of correction, but rather constituted the complete solution. This was a crucial step toward reaching a global solver for whole core calculation retaining the capability to have high local fidelity and leveraging the diffusion operator in such regions as synthetic operator. This work was completed in 2010.

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[1] Texas A&M University

The following years were dedicated to investigating higher order spherical harmonic Sn coupling. Therefore we turned our attention to two-region problems with Sn in one region and P3 (third order spherical harmonics-based approximation) in the other. The first task was to determine a reasonable iteration scheme for the Pn equations, preferably one that bounds the spectral radius away from unity. Two different schemes were investigated and the scheme we selected could be summarized as follows:

1. Perform a Gauss-Seidel iteration in the P3 region using the latest Sn solution at the interface

2. Compute a residual for the Sn iterate

3. Compute a residual for the P3 iterate

4. Solve a global diffusion equation to provide an additive correction to the scalar flux iterates in both the Sn and P3 regions.

This work was completed in 2011. In 2012, both schemes were wrapped in a Krylov solver (GMRES), resulting in improved performance.

In conclusion, this work proved the feasibility to define a coherent overall operator driving the whole core solution (i.e., diffusion or lower order Pn) that could act as a solver where low fidelity is required and act as a preconditioner for a high fidelity solution (Sn) for regions where high fidelity is required. Moreover the difficulties of coupling the different methodologies were specifically addressed and successfully overcome without altering the overall approach.

Benefits to DOE

The challenge to model a full nuclear reactor core to a high level of detail is beyond current computational and mathematical capabilities. This work represents a new approach to such a modeling effort. Classical acceleration schemes are now reformulated as preconditioners in regions of high interest while used as a solver in regions of low interest. This approach could be applied to all multi-scale modeling efforts. Even limiting the application of this approach to the specific case investigated in this project could result in the capability to perform calculations with reduced computational cost and optimized resource usage.

Relevant Publications and Presentations

None.

Fickian and Thermal Diffusion in Nuclear Materials from Linear Response Theory and Multiscale Simulations

Jianguo Yu and Jacob Eapen[1]
10-031

Extending the life of current nuclear reactors and developing next generation reactors requires an understanding of nuclear fuel performance and material degradation in operating regimes where there is very little observational data. Modeling and simulation at the atomistic scale can help accelerate this understanding. This project is developing new statistical-mechanical models and long-time atomistic simulation methods to determine complex diffusive properties in nuclear materials. Specifically, the project aimed to develop state-of-the-art methods to compute Fickian and thermal diffusivities in UO_2 and metallic alloy systems under different thermodynamic conditions.

Summary

Traditional molecular dynamics methods are impractical beyond the nanosecond time scale. Consequently such methods cannot access the slow thermo–diffusion processes in nuclear materials that occur on time scales of microseconds and longer. Accelerated molecular dynamics (a term introduced by Voter and co-workers at Los Alamos National Laboratory) is a technique for extending traditional molecular dynamics approaches to access these longer time scales.

We implemented a theoretical method that computes the thermal diffusion ratio (Soret coefficient) using transition state theory (landscape dynamics). We used Temperature Accelerated Dynamics (TAD)—a type of accelerated molecular dynamics—to compute the thermal diffusion ratio for point defects in UO_2. To our knowledge, this is the first computational work on Soret effect that is based on statistical mechanics and non-equilibrium thermodynamics.

The interatomic interactions between the uranium and oxygen atoms are described using a partially ionic potential model—a combination of Busing-Ida and Morse type potential (developed by Yakub group). After verifying the potential by calculating the basic thermodynamic and kinetic properties, and comparing them against the experimental data (see Figure 1, top), we have quantified the potential energy barriers for points defects (namely, interstitials and vacancies) using TAD. With the known

potential energy barriers, the thermal diffusion ratio is calculated as a function of temperature (see Figure 1, bottom). Note that the most probable transition energy barrier for both the vacancy and the interstitial is independent of T. However, as temperature increases, the number of event occurrences becomes larger.
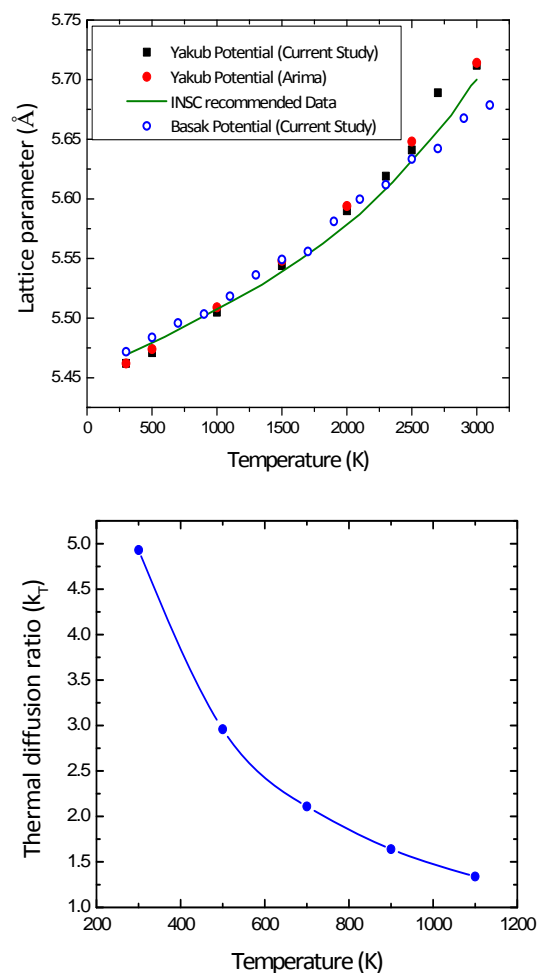

FIGURE 1. Lattice parameters with different potentials (top); thermal diffusion ratio for point defects at different temperatures (bottom).

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[1] North Carolina State University

Benefits to DOE

Our project is central to DOE nuclear security missions. For example, extending the life of the current fleet of light water reactors requires understanding nuclear fuel performance and material degradation in operating regimes where the data is either limited or nonexistent. Modeling and simulation at the atomistic scale can help to accelerate this understanding. Atomistic-scale determination of thermal properties of metallic alloys and uranium oxide fuels will be valuable to the Light Water Reactor Sustainability efforts, the Consortium for Advanced Simulation of Light-Water Reactors, the Center for Materials Science of Nuclear Fuel at INL, and the Fuels Program element of the Nuclear Energy Advanced Modeling and Simulation program.

Relevant Publications and Presentations

Nandi, P., X. Mei, and J. Eapen, "Thermodiffusion in Uranium Dioxide," 2013. (manuscript in preparation)

Eapen, J., "Thermodiffusion in UO$_2$," *Fall MRS Meeting, Boston, MA, November 2012*.

Advanced Visualization Using Immersive Environments

Eric Whiting, William Sherman,[1] Eric Wernert,[1] Amy Banic,[2] Patrick O'Leary,[3] and Aashish Chaudhary[3]
10-094

The ubiquity of immersive environments is increasing. The availability of low-cost virtual reality display systems coupled with a growing population of researchers accustomed to new interface modalities makes this an opportune time to utilize immersive environments and interfaces as part of scientific workflows. However, from past experience we know that having access to equipment is not sufficient. There are multiple barriers to overcome. The first barrier is simply the lack of available usable software that functions well on systems ranging from laptops to high performance supercomputers. Other barriers include a subdued immersion experience or unnatural interactions with data.

This project studied powerful, intuitive, state-of-the-art scientific visualization tools that are appropriate for use in immersive environments. These efforts will enhance and expand the effectiveness and usability of CAES' CAVE[TM] as well as other immersive facilities.

The first objective involved incorporating new immersive features into ParaView, a widely used desktop visualization application from Kitware. The second objective involved a human factors user study of various interaction styles and devices including portable touch input devices, determining implications for both expert and novice users. The outcome of these objectives was a safe and effective mechanism for moving existing scientific analysis and discovery processes into immersive environments. The result of this work is innovative and novel approaches in scientific visualization applicable and important to INL, DOE's Office of Nuclear Energy, and beyond.

Summary

Initial work involved modifications to the underlying software library upon which ParaView is built. These modifications included the addition of off-axis perspective rendering, multi-screen support, dual-viewport stereo mode, configuration file support, and related changes required for proper functioning of Immersive ParaView. Support for interfacing with position tracking and interaction devices was implemented. Work was initiated in preparation for user studies to understand the most effective means of human-computer and human-data interaction in an immersive environment.

During FY 2012, work included developing a deployable version suitable for most end-users as well as adding an intuitive interface to the controls, and the design of a dock panel interface to create the linkages between ParaView server renderers and the input devices. These enhancements were all incorporated into the publicly available code repository for ParaView.

Working demonstrations of Immersive ParaView with both tutorial and INL datasets were created in conjunction with the Kitware team. These were installed in the CAVE at the CAES advanced visualization laboratory.

User study research in the area of 3-D human computer interaction was also conducted in FY 2012 to assess usability and provide guidance to enhance the user experience, facilitate scientific discovery for expert users, and empower novice users through a more natural user interface for immersive applications. The main findings of this research point to the reduction of selection-based errors, as well as the reduction of physical and cognitive demand through the use of touch-based interaction (either with or without direct interaction on a display) or other modifications to existing interaction capabilities. Also, a touch-based display offers users more visibility of the current system state and available options. Although this functionality could be incorporated directly on the immersive display itself, this approach may degrade the overall immersive experience. Additionally, context-switching and task completion time are not affected positively or negatively through the use of touch-based interaction. Other outcomes of this research include, but are not limited to, interface and interaction recommendations for Immersive ParaView and the design and development of a novel touch-based interaction technique.

A large number of disseminations and proposals were developed, and the work was well received by our intellectual community, INL staff, peer DOE national laboratories, and collaborating university partners. This work opens the door to additional scientific visualization work in the CAVE. Given immersive ParaView, almost any researcher can have access to his or her data in a fully immersive display environment. Results from the user studies can affect whether menus and widgets could

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[1] Indiana University

[2] University of Wyoming

[3] Kitware, Inc.

remain consistent across desktop displays to more immersive displays by displaying them on the 2-D touch-based device, thereby offering scalability and portability to visualization applications. As a result of the user experience study and improved interaction techniques, users are more comfortable and more likely to utilize the system for their needs. Therefore, this work enhances and expands the usage and usability of the new CAVE immersive display as well as immersive facilities at other national labs and collaborating universities.

Benefits to DOE

This work is beneficial to DOE's Nuclear Energy Advanced Modeling and Simulation program and as the Consortium for Advanced Simulation of Light Water Reactors Energy Innovation Hub. Results from INL multi-physics codes can be displayed in the CAVE system using these new tools. Work in the CAVE supports the development of technologies to extend the life, improve performance, and sustain the safety of the current fleet of nuclear power plants. This capability helps with design of reactors, fuel cycles, and nonproliferation technologies as well as infrastructure and energy systems. In addition, researchers in related fields at INL have expressed interest in exploring their data using these new capabilities.

Relevant Publications and Presentations

Dhital, A., Z. Sun, N. Areejitkasem, N. Pradhan, and A. Banic, "Evaluation of Touch-Based Interaction and Reduced DOF Input for Widget Control for Immersive Visualizations," *ACM SIGCHI Conference on Human Factors in Computing Systems, CHI 2013, Paris, France, April 27–May 3, 2013.* (submitted)

Pradhan, N. and A. Banic, "Hybrid 6DOF Mobile Interaction for Volume Manipulation in Stereoscopic Display Environments," *RMCWIC 2012 conference, Fort Collins, CO, November 1–2, 2012.* (accepted)

Sun, Z. and A. Banic, "Immersive Visualization in a CAVE? There's An App For That: Mobile Devices as a Universal Medium for Interaction," *RMCWIC 2012 Conference, Fort Collins, CO, November 1-2, 2012.* (accepted)

Sherman, W.R., P. O'Leary, E.T. Whiting, S. Grover, and E.A. Wernert, "IQ-Station: A Low Cost Portable Immersive Environment," *International Symposium on Visual Computing*, Las Vegas, NV, November 29, 2010.

O'Leary, P., "Employing Immersive Environments for Exploration and Analysis in Virtual Nuclear Engineering," *SciDAC 2010, Chattanooga, Tennessee, July 11–15, 2010.*

"Immersive ParaView: A Community-Based, Immersive, Universal Scientific Visualization Application," *IEEE VR, Singapore*, March 19–23, 2011. (submitted)

Shetty, N., A. Chaudhary, D. Coming, W.R. Sherman, P. O'Leary, E.T. Whiting, and S. Su, "Immersive ParaView: A Community-Based, Immersive, Universal Scientific Visualization Application," *IEEE VR, Singapore, March 19–23, 2011.*

Banic, A., "Challenges in Interaction for Immersive Visualizations," *Immersive Visualization Applications Summer Course, CAES, INL, Idaho Falls, ID, July 20–22, 2011.*

Banic, A., A. Dhital, Z. Sun, N. Areejitkasem, and N. Pradhan, "IQ-Station and Touch-Based Interaction with Scientific Visualizations Demonstrations," *University Advisory Board, Idaho Falls, ID, September 21, 2012.*

Banic, A., A. Dhital, Z. Sun, N. Areejitkasem, and N. Pradhan, "IQ-Station and Touch-Based Interaction with Scientific Visualizations Demonstrations," *Engineering Summer Program Research Night, Idaho Falls, ID, June 19, 2012.*

Banic, A., "Interaction for 3D Visualization," *Computer Science Department Colloquium, Colorado State University, Fort Collins, CO, May 2, 2011.*

Banic, A., A. Dhital, Z. Sun, and N. Areejitkasem, "IQ-Station and Touch-Based Interaction with Scientific Visualizations Demonstrations," *Discovery Days, College of Engineering and Applied Science, University of Wyoming, Laramie, WY, March 31, 2012.*

Dhital, A., Z. Sun, N. Areejitkasem, and N. Pradhan, "IQ-Station and Touch-Based Interaction with Scientific Visualizations Demonstrations," *Discovery Days, College of Engineering and Applied Science, University of Wyoming, Laramie, WY, February 18, 2012*.

Banic, A., A. Dhital, and N. Areejitkasem, "IQ-Station and Touch-Based Interaction with Scientific Visualizations Demonstrations," *College of Engineering and Applied Science Open House, College of Engineering and Applied Science, University of Wyoming, Laramie, WY, November 8, 2011*.

Uncertainty Analysis for Multiscale Models of Nuclear Fuel Performance

Michael Pernice, Don Estep, and Simon Tavener[1]
11-074

Developing nuclear fuel cycles that optimize uranium utilization and energy generation, minimize waste and proliferation risk, and increase safety is a principal priority of the DOE Office of Nuclear Energy. Modeling and simulation can help reduce the cost and time required to develop new nuclear fuel forms and to understand the behavior of fuel at high burn-up. There is scant experimental data for the new fuel forms and performance regimes under consideration, which brings the validity of existing empirical models into question. Consequently, a first principles approach to determining properties of materials under radiation is being pursued. This approach uses atomistic calculations to construct a mesoscale description of microstructural evolution of irradiated materials and then upscaling that description to determine material properties that can then be used in engineering-scale models of nuclear fuel performance.

We focus on reliable uncertainty analysis of these multiscale simulations of nuclear fuel performance. Essential elements of our approach include consistent mathematical formulation of the coupled model, a sampling-based approach to coupling the mesoscale and engineering scale, and *a posteriori* error analysis of both the stochastic and deterministic aspects. In addition to accounting for the stochastic behavior of uncertain parameters typical of current approaches to uncertainty analyses, we will also account for numerical error incurred in formulation of the deterministic problem as well as approximation and sampling errors in the stochastic problem.

Summary

The first year goals of this project were to devise a rigorous mathematical foundation for the coupling of the macroscale and mesoscale components of multiscale models of fuel performance and then to devise and implement efficient numerical methods for numerical solution and sensitivity analysis for the coupled multiscale model. The Colorado State University (CSU) team focused on acquiring necessary background in fuel performance models and INL codes and implementing and testing the proposed macro-mesoscale coupling method in a testbed code in Matlab. Specifically, the team visited INL to meet with the INL PI and code developers during this period. In addition to attending the International

Summer School on the Evolution of Microstructural Defects on In-Reactor Material Response at INL, a CSU postdoc carried out a systematic study of background materials related to the modeling of fuel performance. CSU developed and implemented a meso-macroscale modeling method using an intermediate numerical transfer scale, devised a fixed point iteration for the coupling, and studied the convergence. This was done in the context of a simplified stationary model with nonlinear elliptic problems for each scale. The results were very promising. The testbed code was acquired and implementation has begun in C++. At INL, we studied the target mesoscale model application code, MARMOT, in preparation for an initial set of uncertainty analyses and to develop the expertise needed to make modifications to suit our methods.

The primary second year goals of this project were to derive a rigorous mathematical foundation for the coupling of the macroscale and mesoscale components of stochastic multiscale models of fuel performance that includes convergence of the required iteration, implementation of iterative solution method into C++ code, begin export of algorithm to the MOOSE/Implicit Simulation of Nuclear Fuel Computer Code (BISON), and develop an Allen-Cahn stochastic microscale model for use as a surrogate for the more complex Cahn-Hilliard model. Some additional goals such as *a posteriori* error estimation require resolution of these fundamental issues.

The rigorous mathematical foundation has two parts: a theory of solution of a system of coupled stochastic models; and the theory of a mesoscale "layer" that serves for the upscaling and downscaling between the macro and microscales. We have formulated the coupled stochastic system as a system of integral equations for the probability distributions of the coupling variables and proved a general theorem about an iterative solution process for the system akin to a fixed point result. We are now trying to investigate when the assumptions of this result hold in the particular context of the models we are using. We are also making progress in understanding the relation between this result and the analogous results for fixed point solution of the coupled deterministic multiscale system. We have formulated and are currently testing a very exciting innovative description of the mesoscale layer with substantial promise for a mathematical foundation.

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[1] Colorado State University

We derived an Allen-Cahn microscale model and discovered parameter value ranges that provide for mesocale layer behavior, which is a close mimic of the more complicated Cahn-Hilliard model.

We have implemented the algorithm for coupling stochastic macro and micro scale models in a MOOSE/BISON compliant C++ code. We are currently incorporating PETSC into the code to increase efficiency. INL has developed a prototype MOOSE Executioner that can serve to coordinate execution of BISON and MARMOT in our uncertainty analysis.

Benefits to DOE

Multiscale simulation of the performance of nuclear fuel supports several R&D challenge objectives in the DOE Office of Nuclear Energy, in areas such as light water reactor sustainability and alternative fuel cycles. The new analysis capabilities that we develop in this project will lead to improved predictive capabilities for multiscale models of nuclear fuels. The framework that we will develop will also be applicable to other research areas of interest at INL, including carbon sequestration and unconventional fossil fuel recovery, as well as the Advanced Simulation Capability for Environmental Management program in the DOE Office of Environmental Management.

Relevant Publications and Presentations

Breidt, J., T. Butler, and D. Estep, "A Measure-Theoretic Computational Method for Inverse Sensitivity Problems I: Method and Analysis," *SIAM Journal on Numerical Analysis,* Vol. 49, 1836-1859, 2011.

Estep, D., M. Holst, and A. Malqvist, "Nonparametric Density Estimation for Randomly Perturbed Elliptic Problems III: Convergence, Complexity, and Generalizations," *Journal of Applied Mathematics and Computing*, Vol. 38, 367-387, 2012.

Burch, N., D. Estep, and J. Hoeting, "Parameter Estimation and Directional Leverage With Applications in Differential Equations," Metrika, DOI: 10.1007/s00184-011-0358-4, 2011.

Butler, T., D. Estep, and J. Sandelin, "A Computational Measure Theoretic Approach to Inverse Sensitivity Problems II: *A Posteriori* Error Analysis," *SIAM Journal on Numerical Analysis*, Vol. 50, 2012.

Estep, D., V. Ginting, and S. Tavener, "*A Posteriori* Analysis of Multirate Numerical Method For Ordinary Differential Equations," *Computer Methods in Applied Mechanics and Engineering*, 223-224, 2012.

Butler, T. and D. Estep, "A Numerical Method For Solving a Stochastic Inverse Problem For Parameters," *Annals of Nuclear Energy*, 10.1016/j.anucene.2012.05.016, 2012.

Carey, V., D. Estep, and S. Tavener, "*A Posteriori* Analysis and Adaptive Error Control for Multiscale Operator Decomposition Solution of Elliptic Systems II: Fully Coupled Systems," *International Journal of Numerical Methods in Engineering*, 2011. (in revision)

Sheehan, B., D. Estep, S. Tavener, J. Cary, S. Kruger, A. Hakim, A. Pletzer, J. Carlsson, and S. Vadlamani, "The Interaction of Iteration Error and Stability For Time Dependent Linear Pde's Coupled Through An Interface," *Electronic Transactions in Numerical Analysis*, 2011. (submitted)

Chaudhry, J.H., D. Estep, V. Ginting, and S. Tavener, "*A Posteriori* Analysis of an Iterative Multi-Discretization Method For Reaction-Diffusion Systems," *Computer Methods in Applied Mechanics and Engineering*, 2012. (submitted)

Arbogast, T., D. Estep, B. Sheehan, and S. Tavener, "*A Posteriori* Error Estimates For Mixed Finite Element and Finite Volume Methods For Problems Coupled Through a Boundary With Non-Matching Grids," *IMA Journal Numerical Analysis*, 2012. (submitted)

Uncertainty Analysis for Mesoscale Models of Radiation Effects in Materials

Michael Pernice and Anter El-Azab[1]
11-075

Mesoscale modeling—or modeling at nearly the atomic scale—of irradiated materials is used to understand changes to the microstructure of materials in irradiated environments. However, fairly large uncertainties of available material parameters are commonly seen in these models, which could potentially alter the model behavior.

The objective of this project is to conduct uncertainty analysis of a phase-field model for microstructure change in irradiated materials. The work focuses on the void growth phenomenon in pure metals where the growth is controlled by diffusion and reaction of point defects (vacancy and interstitial) produced in materials by irradiation. The mesoscale phase-field model studied in this project is capable of reproducing several experimentally-observed microstructural changes (such as void growth/nucleation, swelling, and gas bubble formation). In order to exploit the predictive capability of this model, it is crucial to quantify the effect of parameter uncertainties on model output.

Summary

The project has two tasks. The first is to carry out an asymptotic analysis of the phase field model whereby the phase-field model parameters are mapped into experimentally measureable physical quantities (or quantities that can be computed from lower scale theory). The second task is then to perform uncertainty quantification (UQ) of the model based on measured/computed parameters.

A simplified one-dimensional asymptotic analysis of the phase-field model was performed following the classic method developed in the context of solidification. Important phase-field model parameters (kinetic coefficient, gradient coefficient, and Cahn-Hilliard mobility) were then related to physical quantities such as surface mobility, surface energy, and defect diffusivity. The analysis also showed that bulk diffusion/sharp-interface void growth rate can be recovered as an approximation of the phase-field model in outer/inner asymptotic expansion. Expression of surface energy in terms of phase-field order parameter is obtained.

Many experiment/computational works on point defects diffusion, surface energy, and defects formation energy were surveyed in order to obtain a reliable set of physical parameters for the purpose of uncertainty analysis.

The technical part of UQ was performed using the Dakota package from Sandia National Laboratory. Newly developed Polynomial Chaos Expansion and Stochastic Collocation methods were used primarily due to their greatly improved efficiency over the traditional Monte Carlo method. Preliminary studies of phase-field model responses for normal-distributed diffusion migration barrier, defects formation energy, and surface energy have been carried out.

Currently, UQ results suggest that—at application-relevant temperature—the effect of surface energy uncertainty is relatively small comparing with the other two quantities, while the effect of formation energy uncertainty to phase-field model response is about the same as the diffusion migration barrier.

Benefits to DOE

By providing a better understanding of the relative parameter importance in the phase-field model, this work will help us achieve predictive modeling for microstructure evolution in irradiated materials. Since the thermal conductivity of nuclear materials is strongly affected by its microstructure, a predictive phase-field model is useful in understanding the evolution of materials thermal property and result in better and more efficient nuclear fuel design, an important goal for both DOE and INL.

Relevant Publications and Presentations

Wang, N., M. Pernice, and A. El-Azab, "Uncertainty Quantification of Micro-Structure Change in a Phase-Field Model for Irradiation Damage," *Computational Materials Science*, 2013. (in preparation)

Nan, W., M. Pernice, and A. El-Azab, "Phase-field Model for Irradiated Materials," *SIAM Conference on Parallel Processing, Savannah, GA, February 2012*.

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[1] Purdue University

Exploratory Nuclear Reactor Safety Analysis and Visualization via Integrated Topological and Geometric Techniques

Diego Mandelli and Valerio Pascucci[1]
11-076

Nuclear energy is a clean, affordable, domestic energy source that has been identified as a key component of the current U.S. energy portfolio. To better understand the safety performance of the aging nuclear reactor fleet, advanced modeling and simulation tools are being used to reduce the need for large, expensive integrated experiments. With the increasing sophistication and accuracy of these simulations, the predictive capabilities are increasingly called upon to inform national policy. In this context, the ability to estimate the likelihood of a given prediction and a quantification of potential uncertainties is crucial. Our approach maps this uncertainty quantification problem to the analysis of functions in high dimensional spaces. We are developing and will demonstrate a new set of mathematical and computational tools for analyzing, visualizing, and interacting with large, high-dimensional data sets that arise in sample-based uncertainty analysis of reactor safety analyses in order to provide better understanding of their inherent structure and how such structure relates to the choice of input parameters of large-scale nuclear simulations.

Summary

In this two and half year project, we are developing an approach that maps the uncertainty quantification problem in large-scale nuclear simulations to the analysis of functions in high dimensional spaces. First, we developed an infrastructure that tests and evaluates the effectiveness of various adaptive sampling techniques for high dimensional scalar functions that are potentially applicable to nuclear simulations. We developed well-understood synthetic datasets for such experiments. Second, we introduced a new class of scoring functions (for adaptive sampling) based on global topological rather than local geometric information. The new scoring functions are competitive in terms of the root mean square prediction error and are expected to better recover the global topological structure of the model. Further testing is needed to understand their full spectrum applicability to nuclear simulations. Third, we developed an analysis and visualization environment for interacting with nuclear simulation data sets that provide a better understanding of their inherent structure. Its extensive capabilities include: (1) interactive persistence simplification of the topology of high dimensional functions, (2) visualization of pair-wise plots that showcase relations among parameters, (3) switching between different global regression techniques, (4) interactive selection of parameters of interest from persistence diagram to provide feedback on input samples involved in features of interest, and (5) inverse inputs plots of data points within each segmented subdomain (i.e., crystal) colored by function values, showcasing confidence of the geometric summary curves and highlighting the existence of outliers.

Furthermore, we developed new interface components for visualizing nuclear simulation data based on hyper-volume visualization techniques. This enables us to provide a fully exploratory, dimension-independent viewing system that scales well with dimension of the data sets. It highlights topological (structural) features from analysis and provides flexibility in manipulating and navigating such features along certain chosen projection dimensions, therefore potentially reveal correlations among different input parameters. We obtained two new sets of simulation data, one with 6 parameters and one with 21 parameters from domain scientists at INL. We modeled these datasets as high dimensional scalar functions and tested them on our prototype software. The prototype software and its user manual was delivered to INL, for testing and exploration. We expect to work closely with the domain scientists and obtain feedback from end users regarding: (1) the interpretation of the testing datasets using our software, (2) the limitations and potential improvements of current analysis techniques, and (3) the potential improvements of the visualization interfaces in terms of usability and interactivity. Given the current progress, we will pursue the following specific deliverables for the period ending in September 2013: (1) complete the development of the current system and improve its robustness, (2) automate the process of selecting important dimensions for analysis and visualization though a combination of machine learning and topological techniques, where the user can then glean important information about these correlations from suggested projections that differentiate large from small topological features automatically, (3) use the current system to extract and visualize the shape of failure regions based on temperature threshold and potentially evaluate their stability for small changes of the temperature parameter. We would further design adaptive sampling techniques that could help in understanding the

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characteristics of the failure regions of the simulation without oversampling the space. Specifically we initially plan to perform adaptive sampling directly on the VR2+ reactor model and to study the topology surrounding the limit surface, (4) compute better approximated topological structures (i.e., Morse-Smale complexes) in high dimensions based on newly developed combinatorial structures (i.e., Empty Region graphs or Witness complexes) and better gradient estimations, and (5) analyze time-varying nuclear simulation data for uncertainty quantification, using both traditional clustering techniques as well as topological segmentations, as complementary tools for data analysis. Further we would like to understand how to select statistics-based and topology-based analysis parameters during such a process. Last, we will extend our existing environment as a monitoring tool that studies the topology of the nuclear simulation data dynamically as new data is being generated.

Benefits to DOE

The latest advances in computational capabilities are enabling the development of computationally intensive simulation codes and the generation of large amounts of data. The ability to analyze and visualize these large amounts of data is essential to understand the underlying process while avoiding incongruences or misunderstandings. This project applies cutting edge methodologies and algorithms to safety analysis codes and data for nuclear systems in order to: visualize the data in an intuitive graphical form; analyze the simulations generated by generic safety analysis codes; and identify correlations between sequence and timing of events and identify system characteristics and limitations using adaptive sampling techniques. These new techniques for visual analysis of uncertainty will provide a unique capability to help analysts explore the high-dimensional landscape of uncertainties in a simulation. This will facilitate risk-informed safety margin characterization of reactor safety and will directly impact light water reactor sustainability. This is the first attempt to develop a comprehensive visualization and analysis tool for generic safety analysis codes. Moreover, special attention will be directed toward the development of adaptive sampling techniques that will help in exploring failure regions of the simulation without oversampling the space. These

computational capabilities will advance the DOE-NE mission and address our nation's ability to develop technologies that extend the life and improve the performance of our nation's current nuclear power plants.

Relevant Publications and Presentations

Maljovec, D., B. Wang, A. Kupresanin, G. Johannesson, and V. Pascucci, "Adaptive Sampling with Topological Scores. Peer-Timo Bremer," *Working with Uncertainty Workshop at IEEE VisWeek, 2011.* (accepted)

Maljovec, D., B. Wang, A. Kupresanin, G. Johannesson, and V. Pascucci, "Adaptive Sampling with Topological Scores. Peer-Timo Bremer," *International Journal for Uncertainty Quantification, 2012*. (accepted)

Wang, B., B. Summa, V. Pascucci, and M. Vejdemo-Johansson, "Branching and Circular Features in High Dimensional Data," *IEEE Transactions on Visualization and Computer Graphics*, Vol. 17, 1902-1911, 2012.

Exploration of High-dimensional Scalar Function for Nuclear Reactor Safety Analysis and Visualization SCI technical report UUSCI-2012-005, 2012.

Maljovec, D., B. Wang, A. Kupresanin, G. Johannesson, P.T. Bremer, and V. Pascucci, "Adaptive Sampling with Topological Scores," *Working with Uncertainty Workshop at IEEE VisWeek 2011*, Providence, RI, October 24, 2011.

Wang, B., B. Summa, V. Pascucci, and M. Vejdemo-Johansson, "Branching and Circular Features in High Dimensional Data," *IEEE Visualization 2011 Conference,* Providence, RI, October 23–October 28, 2011.

Maljovec, D., B. Wang, A. Kupresanin, G. Johannesson, V. Pascucci, and P.T. Bremer, "Adaptive Sampling with Topological Scores," *Fields Institute for the Thematic Program on Discrete Geometry*, Toronto, Canada, November 7–11 and November 14–18, 2011.

Maljovec, D., B. Wang, A. Kupresanin, G. Johannesson, V. Pascucci, and P.T. Bremer, "Adaptive Sampling with Topological Scores," *SAMSI Uncertainty Quantification Transition Workshop*, Durham, NC, May 21–23, 2012.

Multiphase Flow Modeling Capability for Waste-to-Energy Process Development

Donna Post Guillen
12-100

This project explored new methods for 3-D visualization using computational multiphase fluid dynamic (CMFD) simulations. An OpenFOAM (an open source fluid dynamics tool) simulation of a bubble column was used as a test case for the development of new illustrative visualization methodologies. Visualization of time-varying CMFD data is challenging due to the nature and size of the datasets. Research was performed to convey information to the viewer using non-traditional methods. The ultimate vision for this work is to create a "Virtual Laboratory" environment, where the user interacts with a multi-model, tele-immersive virtual reality environment. Currently available massively parallel supercomputers provide sufficient performance to simulate multi-dimensional, multi-variable problems in high resolution. Especially for complex models, visualization is key to understanding the interacting physico-chemical processes occurring in the system. Such virtual objects can be displayed in INL's CAVE™ by taking advantage of high-quality rendering, stereoscopic displays, and interactive navigation and tracking.

Conventional visualization techniques tend to employ photo-realistic and physically-motivated approaches to the presentation of simulation data. While such approaches yield accurate visualizations, the generated data representations are often difficult to interpret—especially with the increasing scope and complexity of simulations. For example, dense vector or stream surface plots can overwhelm an observer with data, and depth information may be lost when projected to 2-D. The field of illustrative visualization has developed as a response to the challenge of presenting complex simulation data, and proposes the application of techniques developed in the history of scientific illustration. In this paradigm, the objective is to employ compact and intuitive representations to convey key details of simulations qualitatively.

Summary

MarmotViz, a generalized framework for illustrative visualization, has been developed and implemented as a ParaView plug-in, enabling its use on a variety of computing platforms with various data file formats and mesh geometries. MarmotViz incorporates a number of prominent algorithms and techniques found in the literature, and its flexible architecture supports the rapid implementation of new illustrative visualization functionality. It enables users to identify and track time-varying *features* in simulation datasets. It permits the application of illustrative visualization effects to these features including: selective visualization, feature coloring, boundary smoothing, haloing, silhouette outlining, speedlines, and strobe silhouettes. These effects, applied to a CMFD simulation of a bubble column, are shown in Figure 1. These techniques serve to assist in exploration and interpretation of simulation data and can be used to generate enhanced renderings for presentations. MarmotViz can be easily extended to incorporate new region-of-interest (ROI) identification algorithms, feature matching and tracking algorithms, and illustrative visualization effects.
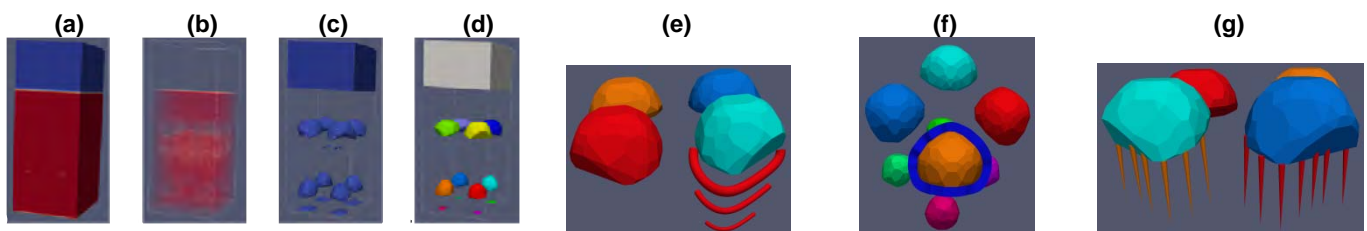
FIGURE 1. 3-D visualization of: (a-d) bubble column simulation, (e) strobe silhouettes, (f) haloing, and (g) speedlines.

MarmotViz is currently the only general-purpose illustrative visualization plug-in available for ParaView. MarmotViz is a uniquely flexible framework, enabling rapid development and incorporation of new illustrative visualization algorithms and effects. MarmotViz implements a number of illustrative visualization techniques found in the literature as well as novel algorithms and approaches, which include:

- *Adaptive volume feature tracking*—This algorithm is used to match and track features using volume and velocity data. The matching criterion is adaptively relaxed, enabling rapid matching of nearby similar feature instances followed by less-similar feature instances.

- *Generalized boundary silhouette identification*—This algorithm is used to identify a view-dependent bounding contour around a contiguous ROI. It supports ROIs constructed from general 3D elements (tetrahedra, hexahedra, wedges, etc.). This bounding contour information is useful for various illustrative visualization effects.

- *General illustrative visualization pipeline*—MarmotViz is structured to support the use of general ROI identification and feature matching algorithms, enabling its application to a wide variety of datasets. Additionally, it permits the selective application of general illustrative visualization effects to individual features.

Alexander Rattner, a Ph.D. student from Georgia Institute of Technology was supported by a DOE computational science graduate fellowship to assist with this LDRD project. This work is ground-breaking in that the illustrative-inspired techniques put into practice here have not been previously applied to computer simulations of fluid flows. We have submitted MarmotViz copyright paperwork to the INL Technology Deployment organization.

Benefits to DOE

This project is exploring advanced visualization and modeling techniques. The applications of these techniques are far reaching and encompass scientific disciplines such as medicine, engineering and the natural sciences. Modeling and visualization are important parts of all energy-related science fields and especially contribute to nuclear energy research, a key part of DOE's energy security mission.

Relevant Publications and Presentations

Guillen, D.P., "MarmotViz: an Illustrative Visualization Framework for Time-Varying Simulations in ParaView," *OpenFOAM User Meeting, Pittsburgh, PA, October 20, 2012.*

Guillen, D.P., Demo to General Electric, Idaho National Laboratory CAVE, Idaho Falls, ID, August 7, 2012.

Guillen, D.P., "Generalized Framework and Algorithms for Illustrative Visualization of Time-Varying Data on Unstructured Meshes," *Computers and Fluids,* 2013. (in preparation)

INSTRUMENTATION, CONTROL AND

INTELLIGENT SYSTEMS

Automated Differential Equation-Based Identification

Lee Shunn, Craig Rieger, and Charles Tolle[1]
10-014

Modern control systems are the central nervous system for critical infrastructure, which includes a host of other technologies. These control systems have become enabling technologies for the mission success of all industries worldwide. This project is developing and demonstrating a new class of algorithms for nonlinear system identification (sys-ID) to provide the foundation for "on-the-fly" prognostics and control techniques to allow a control system to be resilient. Sys-ID relates to building mathematical models of dynamical systems based on observed input-output data. For the case of linear models, there are well-structured theories, methodologies, and algorithms to construct the relationships. For complex nonlinear models, however, general techniques are not as established or robust. However, trajectory techniques found in the literature provide promising methods to reconstitute the complex nonlinear models and add dynamic evolution of the models being fit back into the system identification problem. The resulting objectives for this project are based upon application of these methods:

- Extend the sys-ID method and tools to support high-dimensional systems

- Incorporate forcing terms into the sys-ID method

- Automate basis function selection using a genetic algorithm (or other suitable approach)

- Explore mapping functions that can cleanly transform embedded dynamics to the original phase space

- Apply sys-ID tools to problems of interest at INL.

Summary

There are several differences between the current method and other available sys-ID techniques. Discrete-time autoregressive models (e.g., AR, ARMA, ARX, ARMAX) use past values from a time series to predict future values. The resulting relationships are typically linear, although some nonlinear variants exist. Transfer function models use linear dynamics and time-delays to approximate nonlinear systems. This approach can result in cumbersome expressions in the Laplace domain whose physical interpretation can be problematic. Hammerstein-Wiener models offer a convenient framework to parameterize some nonlinear features.

However, all such models have a linear transfer function at their core and use a nonlinear transformation on the input and output to describe the nonlinearities. While all of these methods can provide predictions of the system's outputs y, none offer a description of the internal state variables x. Discrete-time state-space models offer a description of both the state variables and outputs. However, current implementations only allow for linear analysis. The present approach provides a complete state-space description of nonlinear systems (including the outputs and state variables) in the time domain.

A new C++ code was written to include arbitrarily high-dimensional systems (restricted only by the physical limits of the computer hardware). Collaborators at the South Dakota School of Mines and Technology (SDSMT) completed the coding, debugging, and validation of the code. The new implementation frees this work from commercial software packages such as MATLAB, and creates a faster stand alone tool with a high degree of portability.

Previous implementations of similar methods in control systems do not permit a straightforward description of the interaction of the system with the control actions. The new sys-ID code includes explicit forcing terms and a unique "cross-term" contribution, i.e., $dx/dt = A(x(t)) + B(u(t)) + C(x(t),u(t))$, where $u(t)$ represents external forcing by the controller.

Work by the team at SDSMT identified the Moore-Penrose pseudo-inverse as a promising transformation between the original manifold (attractor) and the manifold defined by a time-delay embedding. Coefficients in the transformation have been optimized using a random walk algorithm to produce a "best-fit" linear mapping. Work to optimize simple nonlinear mappings and numerically demonstrate Taken's embedding theorem is being drafted for a journal paper.

An approach to fully automate the selection of basis functions for analysis of systems using a genetic algorithm and a novel grammar-based function evolution process is being developed. The code for this grammatical evolution has been written and tested and the process of coupling it to the sys-ID code will continue under a follow-on grant to SDSMT from the Office of Naval Research.

Several applications have been identified as targets for the sys-ID method. The project completed two

demonstration experiments at SDSMT as test beds for method validation – a radially driven inverted pendulum system, shown in Figure 1, and a linearly driven inverted pendulum system, shown in Figure 2. These experiments are simple enough to generate clean, manageable data, yet complicated enough to be interesting and relevant to "real" systems. The SDSMT collaboration has led to potential sys-ID demonstrations using data from a SAE Baja racer, flight data from a quad-rotor helicopter, and the INL HYTEST (Hybrid Energy Systems Testing) dynamics lab.
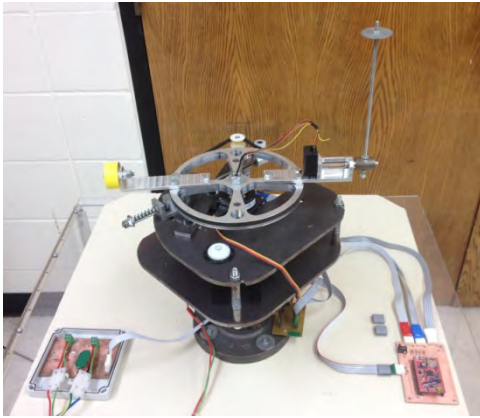
FIGURE 1. Radially driven inverted pendulum system.
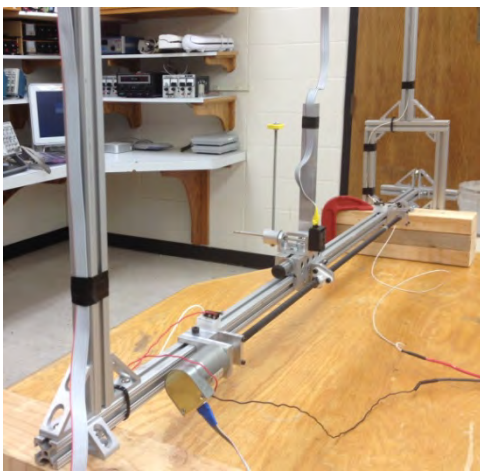
FIGURE 2. Linearly driven inverted pendulum system.

Benefits to DOE

This research will contribute to DOE's goal for energy security by enabling the deployment of resilient control systems for the power grid and other infrastructure through the advancement of highly adaptable systems for prognostics and control. This project provides valuable contributions to applied sys-ID as well as dynamical systems theory and chaos. Developments have been communicated through peer-reviewed journal articles and conference presentations, enhancing DOE and INL's technical standing in the instrumentation and controls community.

Relevant Publications and Presentations

Tolle, C.R., "Musings on Persistent Excitation Prompts New Weighted Least Squares SysID Method for Nonlinear Differential Equation Based Systems," *IEEE 5th International Symposium on Resilient Control Systems, Salt Lake City, UT, August 2012*.

Tolle, C.R., R. Hoover, and C. Rieger, "A Linear Approximation to the Embedding Theorems: The Search for a Near Linear Diffeomorphic Mapping," *SIAM Journal on Control and Optimization*, October 2012. (in preparation)

Tolle, C.R. and R. Hoover, "Adding Dynamics Back Into SysID," *IEEE Black Hills Subsection Meeting, Rapid City, SD, September 13, 2012*.

Tolle, C.R. and R. Hoover, "A Linear Approximation to the Embedding Theorems: The Search for a Near Linear Diffeomorphic Mapping," *South Dakota School of Mines & Technology IEEE Student Branch Meeting, Rapid City, SD, April 2011*.

3-D Spatial Representation in Support of Design Inspection and Verification

Mark McKay, David Gertman, Richard Metcalf, Robert Kinoshita, and Kelly Michel[1]
10-029

In light of the international concerns over misuse of nuclear materials and often-limited access to facility information and inspection time in facilities, this project provides a novel information fusion/visualization solution to allow a safeguards inspector to efficiently baseline, analyze, and recognize potentially anomalous nuclear facility configurations.

Across the globe, nuclear facilities are subject to safeguards via the International Atomic Energy Agency (IAEA), who perform inspections to verify that facilities of interest have not been altered to allow misuse or diversion of special nuclear material. When inspecting a facility, IAEA inspectors complete a design information verification (DIV) that relies heavily on inspector knowledge, experience, and analysis of volumes of facility information that encompasses photographs, blueprints, sketches, drawings, plots, diagrams, notes, and documents. In preparing for a DIV, inspectors are faced with the fundamental difficulties of translating facility documentation of relevant safeguards systems and practices, and then spatially correlating relevant safeguards information into the facility physical design.

To lessen the workload on a safeguards inspector, this project focused on developing a prototype, hand-held/wearable system that integrates facility information, personal odometry system, and a 3-D virtual graphical user interface into a facility information system (FIS). The prototype (see Figure 1) was developed to intuitively aggregate data storage and spatial registration of facility information, coupled with extraction of the relevant information on demand. Inspectors can interact with the FIS through a 3-D digital replication of the facility to pinpoint facility aspects of interest.

The 3-D virtual environments (VE) provide rich visual cues, but evidence suggests visual information alone is not sufficient to adequately navigate a VE effectively. Therefore, INL developed a positioning solution for accurately tracking human movement in GPS-denied areas and use this position information to auto-register the VE perspective to that of the human operator in the physical work.
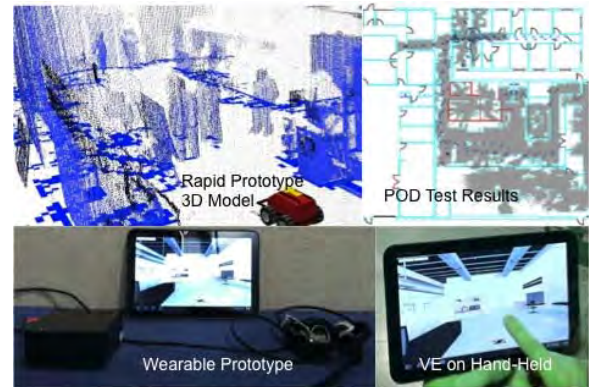
FIGURE 1. Prototype Overview.

The work provides facility inspectors with a useful toolset and advances nuclear nonproliferation and instrumentation and controls core capabilities of INL. Solving challenges associated with development of this toolset also provides novel contributions in: (1) task analysis of inspector roles, responsibilities, and information requirements, (2) rapid VE modeling of other industrial facilities; position correlation from physical to virtual environment, (3) Human Computer Interaction research, and (4) Training aid for new generations of industrial plant operators and dispatchers.

Summary

Year one activities focused on obtaining the baseline parameters for the DIV design, developing models and the database design, which were addressed with the following accomplishments: (1) completed the human task analysis of a DIV inspector by soliciting a former IAEA DIV Inspector, (2) designed a DIV database to contain information pertinent to the DIV task, (3) updated the Virtual Model of the INL's Fuel Conditioning Facility to be spatially accurate, and (4) modeled an INL facility as a program testbed.

In year two, we developed rapid modeling tools and VE interface for presentation of the facility information for a human factors evaluation. The accomplishments are: (1) coupled the inertial position tracking system to the VE

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camera perspective, (2) published a conference paper outlining our progress to date at the Institute of Nuclear Materials Management, (3) hired two interns to support the project, a Human Factors specialist from the University of New Mexico, and Chemical Engineering undergrad at Montana State University, (4) developed Rapid Modeling Prototyping tools utilizing robot systems and laser range finders to collect facility data into a sub-centimeter accurate point cloud that is viewable through a web browser or the Center for Advanced Energy Studies' CAVE[TM], and (5) developed the mobile-based VE interface used to display the 3-D facility model in a prototype hand-held tablet computer.

In year three, we continued to define and refine the FIS design and ease of usability of some of the key components, as well as making the design less intrusive to operate or carry by investigating the possibility to minimize external sensors. Some specific accomplishments included: (1) refined the rapid modeling prototyping tools utilizing robot systems and laser range finders improving the ease of usability and 3-D map creation. Evaluated tools for down selecting and converting point-cloud data to polygon based 3-D models, (2) collected design engineering tests results with the indoor personal odometry system, and (3) investigated the use of onboard hand-held mobile device sensors for indoor position tracking in GPS-denied areas. Initial results indicate it may be possible to track a user's position solely from the onboard device sensors.

Benefits to DOE

This project has benefitted the DOE and national nonproliferation missions by developing a toolset to enable international safeguards inspectors. This toolset will make inspectors more prepared prior to inspections and provide better real-time situational awareness to improve the effectiveness of inspections by reducing

uncertainties in facility configurations and safeguards systems. Additionally, the prototype tools can be modified to assist nuclear plant operators in documenting and tracking maintenance, upgrades and operations. Finally, this toolset can meet Department of Defense and State Department requirements for technologies that can require photorealistic virtual or augmented reality environments in near real-time, where rapid evaluation of facility configurations can be performed to aid in modification and design analysis.

This project is aligned with INL's strategic R&D objectives to "Understand and minimize risk of nuclear proliferation and terrorism" and "Discover, develop and deploy innovations that advance critical infrastructure systems." The project's objectives and technical progress were validated to be aligned with national needs when presented at the 51st Annual Meeting of International Nuclear Material Management. In addition, in an effort to continue this work, we submitted a white paper and full proposal to the National Nuclear Security Administration, Sponsor Organization NA-22.

Relevant Publications and Presentations

Few, D.A., D.I. Gertman, K. LeBlanc, K. Michel, and B. Hayes, "Augmented Reality: Don't We All Wish We Lived In One?" *roc. of the Institute of Nuclear Materials Management 51st INMM Annual Meeting,* Baltimore, MD, July 2010.

McKay, M. "3D Spatial Representation in Support of Design Inspection and Verification," *Instrumentation, Control, and Intelligent systems Distinctive Science Signature Review, Salt Lake City, UT, August 13, 2012.*

Resilient Condition Assessment Monitoring (ReCAM) System

Humberto Garcia, Wen-Chiao Lin, Semyon Meerkov,[1] Kameshwar Poolla,[2] and Annarita Giani[3]
10-037

A "smart" power grid—and other advanced infrastructure systems that use sensors—will require a resilient infrastructure monitoring system that enables *graceful degradation* (rather than collapse) when faced with natural or malicious sensor malfunctioning. One of the main goals of this project is to develop algorithms that implement the notions of information quality (IQ) and assessment quality (AQ) that can be used on-line to reconfigure monitoring systems based on the assessed conditions of a monitored process. In particular, we envision that the developments in this project, complex engineering systems can be reliably monitored to ensure safety and proper operations. The monitoring algorithms considered here offer challenging objectives for efficient processing of information and correct assessment of facility health (both physical and cyber) within operational variances that include natural or malicious disturbances. Specifically, we are evaluating novel resilient monitoring approaches that drive data needs according to possibly time-varying AQ/IQ conditions, resulting in the capability to autonomously select sensors for a monitoring system that marshals data as performance requirements change or gracefully degrade under natural and malicious perturbations (e.g., cyber-physical attacks), even under severe sensory loss. With an emphasis on monitoring systems, objectives for this project include:

- Develop novel technologies focusing on the "monitoring" aspect of resilient systems. This objective includes formulating and integrating innovative notions (e.g., IQ, AQ), architectures, and methodologies.

- Demonstrate these developed resilient monitoring technologies on facility-level multi unit applications.

- Advance concepts that integrate physical security, cyber security, monitoring stability and efficiency, data fusion, and state awareness into resilient system dashboards.

Summary

In this project, we are assuming a set of sensors is used to observe a monitored plant, where there may be natural or malicious disturbances to the sensors and plant. We are also assuming data from each sensor are accompanied by a level of IQ, which includes data quality (DQ) indicating trustworthiness of the sensor data, and data relevance, indicating usefulness of the sensor data. Different approaches may be used to generate sensor DQ. For instance, a watch dog system may monitor data traffic pertaining to a particular sensor and assign low DQ to this sensor if abnormal data traffic is detected. For applications to power grids, we used state estimation techniques to develop algorithms that assign sensor DQ based on residuals calculated from measured and estimated state variables. We also developed an active probing technique that assigns DQ of a sensor based on consistency of sensor measurements with probing results. The sensor data along with their associated DQs are then used in ReCAM.

The structure of ReCAM consists of three layers: *information*, *assessment*, and *sensor selection.* In the information layer, sensor data and DQs are used to calculate process variable (PV) probability distributions. These calculations are combined based on Dempster-Shafer theory if more than one sensor is active in observing a particular process variable. In order to prevent abrupt changes to PV estimations, calculated PV probability distributions are then fed as inputs to a smoothing process to estimate of PV probability distributions. The estimated PV probability distributions are then used in the assessment layer to assess the condition of the plant.

At the assessment layer, estimations of PV probability distributions are used as soft evidence for calculating the probability distribution of plant assessments. These calculations are based on probabilistic reasoning methods, and, in particular, Bayesian belief networks (BBN). The BBN is used repeatedly with prior probabilities set as the updated plant assessments from the previous time instant. The entropy (indicating the confidence) of the assessment probability distribution is subsequently calculated. If this entropy is lower than a user-defined threshold (indicating required confidence on assessments), a definite decision on the plant status is made based on the plant assessment probability distribution and then the assessment process repeats (with prior probabilities in the BBN set to complete ignorance, i.e., uniform distributions). If not, a predicted

decision period—which is an estimated time between the last and next definite decision of the plant status—is computed. Based on the difference between the predicted and desired decision periods, which depends on previous plant assessments, penalties are generated for sensor selections to accordingly adjust sensor configurations for meeting the desired decision period within pre-determined tolerance.

At the sensor selection layer, sensor selections are based on current sensor DQs, power grid health assessment qualities, predicted monitoring performances, and predicted cyber-physical attacks. Several benefits can be afforded by this time-varying sensor selection, including making it harder for an attacker to inflict a successful attack. Selecting a subset of sensors based on assessed sensor DQs also reduces the risk of using an attacked sensor. Furthermore, more sensors can be selected as needed if a physical anomaly is detected (i.e., marshalling data as driven by assessed health conditions). Two mechanisms work together for selecting sensors. The first is based on a zero-sum, two-person game theoretic framework, while the second uses adaptive algorithms based on the theory of rational behavior, for dynamic sensor selections. Calculations based on the former

provide best sets of candidate sensors to be selected based on the latter. Compared to sensor selection methods that do not use sensor sets suggested by game theoretic calculations, simulation studies using a simplified power plant model show that, with game theoretic calculations, monitoring performance of ReCAM can improve as much as 35.96% when sensor DQs do not accurately reflect the cyber attacks.

ReCAM was also applied to a power grid (i.e., an IEEE [Institute of Electrical and Electronics Engineers] 300-bus test case). In particular, sensor DQ calculations are based on comparisons between reported sensor signals and those from power grid state estimations. Physical anomalies currently considered are increase of resistances of power grid branches, while the cyber attacks considered are false data injection (e.g., adding bias) to sensors. It is shown that ReCAM is able to detect and diagnose power grid physical anomalies despite cyber attacks to 33% of deployed sensors.

As indicated in Figure 1, ReCAM provides features such as disturbance characterization and look-ahead prediction, prediction modeling, and alternative analysis, damage and risk avoidance, and rational adaptation.
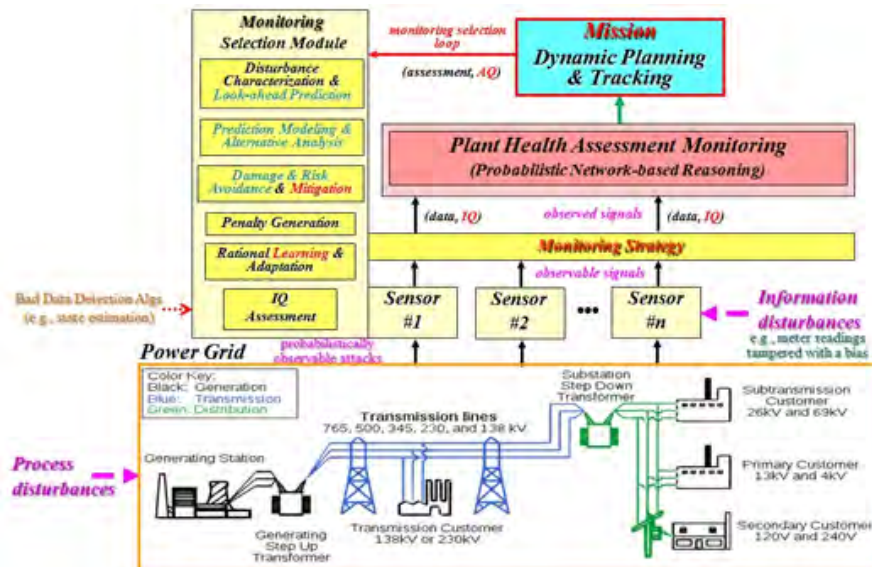
FIGURE 1. Illustrative application of ReCAM to (smart) power grids and ReCAM features.

Benefits to DOE

This research develops scientific- and engineering-based techniques supporting DOE mission objectives for establishing resilient infrastructures that operate under natural and malicious perturbation to sensors and physical assets. This project has demonstrated the potential to enable the resilience of an electric power grid monitoring system that is applicable to future power plants and the Smart Grid, where a large amount of sensors are deployed and may be subject to off-normal events.

Relevant Publications and Presentations

Garcia, H.E., W-C. Lin, S.M. Meerkov, and M.T. Ravichandran, "Data Quality Assessment: Modeling and Application in Resilient Monitoring Systems," *Proceedings of the 5th International Symposium on Resilient Control Systems*, *Salt Lake City, UT, 2012*.

Garcia, H.E., W-C. Lin, and S.M. Meerkov, "A Resilient Condition Assessment Monitoring System," *5th International Symposium on Resilient Control Systems*, *Salt Lake City, UT, 2012*.

Garcia, H.E., N. Jhamaria, H. Kuang, W-C. Lin, and S.M. Meerkov, "Resilient Monitoring System: Design and Performance Analysis," *4th International Symposium on Resilient Control Systems*, *Boise, ID, 2011*.

Garcia, H.E., W-C. Lin, S.M. Meerkov, and K. Poolla, "Resilient Condition Assessment Monitoring (ReCAM) System," *ICIS External Advisory Committee Review, Salt Lake City, UT, August 13, 2012*.

Garcia, H.E., W-C. Lin, S.M. Meerkov, and M.T. Ravichandran, "Data Quality Assessment: Modeling and Application in Resilient Monitoring Systems," *5th International Symposium on Resilient Control Systems*, *Salt Lake City, UT, 2012*.

Garcia, H.E. and W-C. Lin, "Complexity and Graceful Degradation: ReCAM & ReMAC Systems," *Energy Security and Resilient Control Workshop*, University of *Southern California, Information Sciences Institute, Los Angeles, CA, November 2011*.

Garcia, H.E., "Resilient Condition Assessment Monitoring (ReCAM) System: Architecture, Design, and Performance Analysis," *Haythornthwaite Lecture Series*, *Temple University, College of Engineering, Philadelphia, PA, 2011*.

Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State

Miles McQueen, Milos Manic,[1] Ondrej Linda,[1] Kameshwar Poolla,[2] and Annarita Giani[3]
11-046

This research is an investigation of a low cost, accurate, and reliable mechanism for detecting manipulation of critical physical processes and falsification of system state in control systems for infrastructure. We call this novel mechanism "Known Secure Sensor Measurements" (KSSM). The method moves beyond analysis of network traffic and host based state information, and uses physical measurements of the process being controlled to detect falsification of state. KSSM is intended to be incorporated into the design of new, resilient, cost effective critical infrastructure and associated control systems. Perhaps more importantly, it can also be included in incremental upgrades of already installed infrastructures and systems for enhanced resilience. KSSM is based on "known secure" physical measurements for assessing the likelihood of a cyber attack and is intended to demonstrate a practical approach to creating, transmitting, and using the known secure measurements for detection.

Summary

Our research assumed that the attacker can compromise any of the components in the information layer of a control system without being detected as long as the attacker does not modify the sensor signals being transmitted back to the controller and the control room. KSSM is not designed to detect the system process exceeding its operational performance envelope, normal system monitoring is expected to detect that situation. Rather, KSSM is designed to reliably detect any attempt to falsify system state through manipulation of one or more of the sensor measurements being reported back to the control room.

In 2011 we conceptualized a design of a KSSM system for general systems, and identified the most important components. The KSSM module residing in the control room is represented in Figure 1. It is responsible for modifying the subset of KSSM-enabled sensors which perform encryption, and is also responsible for detecting attacks. Many functions are needed to provide these capabilities and a few of the highest level functions will now be briefly described.
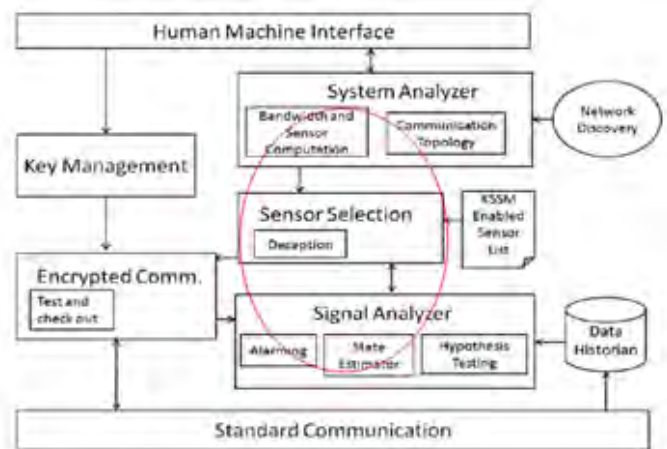
FIGURE 1. Core components within the Control Room KSSM module.

The system analyzer receives input from network discovery tools that can both reside on the system and operate in real time, or serve as one-time-only devices used during a phase such as system acceptance testing. The system analyzer develops simplified models of the communication network to aid the sensor selection function in choosing smart subsets of sensors. The signal analyzer is responsible for analyzing the sensor measurements that are provided to the control room, and alarming when appropriate. The sensor selection algorithm incorporates what is known about the communication topology and the failure rates of all components within the system. The failure rates may be based on empirical data or models built into the algorithm. Further, some understanding of the limits on computation cycles available, sensor power restrictions, limitations in communication bandwidth, and cost are incorporated to aid—not only the selection of a new subset of sensors for KSSM—but also the selection for each chosen sensor of the k_i of measurements that will be encrypted and forwarded.

In evaluating these various functions we decided to focus on sensor selection algorithms since we believed it was the most significant issue which might impede the viability of the KSSM concept. Initially, we decided to look at placement of a small set of Phasor Measure Units (PMUs) (phase and magnitude measurement at relatively high rates for the grid) within the power grid recognizing that it is the equivalent of selecting an optimal set of p PMUs if a

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[3] Los Alamos National Laboratory

much larger set of N were available. We first introduced and characterized irreducible cyber attacks on the power grid which is represented as a general graph (Figure 2). We developed an efficient algorithm to find all irreducible attacks that involve the compromise of exactly two power injection meters. We also derived canonical forms for all 3-, 4-, and 5-sparse attacks under the assumption that all lines are metered. We then developed countermeasures against arbitrary unobservable attacks using known-secure PMUs, and shown that PMUs are sufficient to disable p-1 attacks.
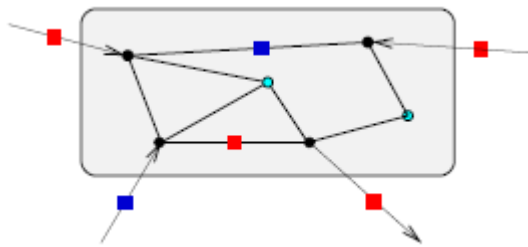
FIGURE 2. General power system represented as a graph with edges representing lines and nodes representing buses. Injection buses are black circles, null buses cyan circles, meters blue squares, and compromised meters red squares.

In parallel with PMU placement we developed simulations to study sensor selection algorithms for more general physical processes. Initial and relatively simplistic network models were developed and used to test a few techniques for sensor selection and alarming. The results were positive and reflect the feasibility of applying KSSM concepts to systems beyond the power grid.

In 2012 we addressed the problem of optimal selection and placement of Known Secure Sensors in the power grid. For our primary case study, we focused on multi-criteria/multi-stage placement of PMUs in the grid taking into account observability, cost, reliability, and security. Security was evaluated using FY 2011 and new FY 2012 results related to using PMUs to detect sparse data integrity attacks in the power grid.

We created and evaluated the application of a memetic algorithm for use in optimizing the multi-criteria/ multi-staging of PMUs. We then extended the algorithm by using Type-2 fuzzy logic to aid evaluation of various PMU placements and staging into the grid. Figure 3 and

Figure 4 reflect two different scenarios for staging and placement of PMUs in the IEEE 30-bus system. In the first scenario security is weighted by the decision maker as having little importance while in the second scenario the decision maker has decided that security is the most important factor. Figure 3 is a Vornoi diagram visualization of the two scenarios. Dark red represents the most important PMUs according to the multi-criteria evaluation while light green represents the least important PMUs. Figure 4 clearly demonstrates that when security is considered more important than observability, then sparse data integrity attacks are addressed much earlier in the staging process. After the first two PMU placements, all sparse data integrity attacks are detectable.
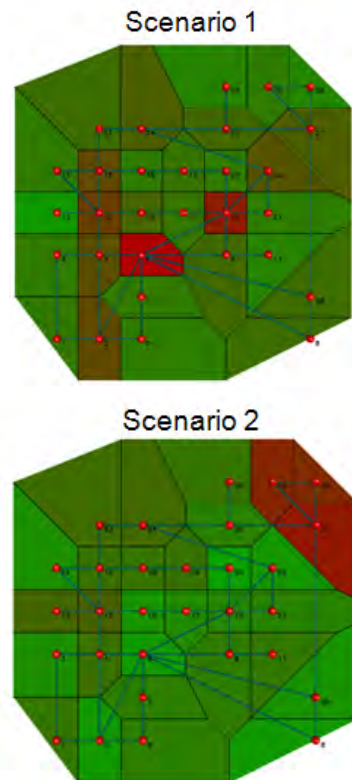
FIGURE 3. Vornoi diagram visualization of scenario 1 where observability is most important and scenario 2 where security against sparse data integrity attacks is most important. Dark red represents the most important PMUs while light green represents the least important.
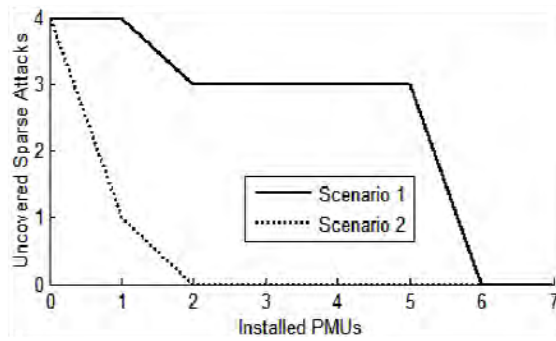
FIGURE 4. With security weighted low (scenario 1) the ordering of PMU staging is such that it takes quite a few installed PMUs before all sparse data integrity attacks are covered. When security is weighted high (scenario 2) the PMUs which mitigate sparse data integrity attacks are ranked higher in order of placement and thus all sparse attacks are covered after the first two PMU placements.

In addition, in 2012 we began to develop first order methods for assessing the damage data integrity attacks could impose on the grid through misleading operators into making inappropriate decisions. We are using these initial results to develop metrics to assess the economic impact of these attacks under operator re-dispatch decisions using optimal power flow methods. These metrics can be used to enhance the prioritization of PMU placement in the grid. In addition, these metrics are intended to be used to aid prioritization of other security sensors and mechanisms.

Benefits to DOE

This research is establishing scientific- and engineering-based techniques for improved and reliable detection of cyber attacks against infrastructures and their associated control system processes—a key component of energy security. The techniques are based on control system specific "known secure" physical measurements that are not available in IT-based detection mechanisms and have not been generally incorporated into infrastructure control system cyber security attack detection tools. The research has focused on multi-criteria/multi-stage optimal placement of PMUs

within the power grid to detect an attacker's falsification of system state. Initial algorithms for PMU placement have been created and validated with simulations on small and medium sized grids. More general infrastructure control systems and their corresponding infrastructures have also been investigated and the feasibility of the core KSSM concepts evaluated using initial simulations.

Relevant Publications and Presentations

These presentations are for 2012 only.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *Energy Security and Resilient Control Systems Workshop, Marina del Ray, CA, November 15, 2012*.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *Fujitsu Laboratories of America, Sunnyvale, CA, February 1, 2012*.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *Cyber Physical Systems Week, Beijing, China, April 16, 2012*.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *San Diego, CA, July 2012*.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *Independent ICIS-KSSM External Research Review, Salt Lake City, Utah, August 13, 2012*.

McQueen, M. and A. Giani, "Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State," *Conference Paper Presentation, Lillehammer, Norway, September 17, 2012*.

255

Battery Resilient Monitoring and Control

Jon Christophersen and Humberto Garcia
12-071

INL is collaborating with Montana Tech of the University of Montana to develop a novel sensor technology that can rapidly acquire impedance spectroscopy measurements of energy storage devices. Studies at INL have examined the effectiveness and long-term impact of this novel sensor. Batteries and other energy storage devices are becoming increasingly important for several industries—including automotive, electric utilities, and military applications. Increased performance requirements, combined with the high cost of energy storage devices, emphasize the need for improved battery management systems that accurately assess the overall state-of-health (SOH) and remaining useful life (RUL). Impedance spectroscopy has been emphasized as a valuable tool for battery modeling and accurate life estimation.

In this effort, the objective was to develop a proof-of-concept for a battery SOH metric and a smart algorithm that optimizes battery management based on current and projected usage. Data from the validation studies are used with empirical models to estimate and predict battery SOH and RUL given an impedance spectrum at a known temperature and state-of-charge (SOC). The model can then be combined with other passive measurements (voltage and current) to form a more complete battery health metric. Once a more thorough health metric has been identified, it can be used by the battery management system to optimize usage based on its current SOH and predicted RUL. Present

SOH assessment techniques typically focus on simple, passive measurements from which capacity, energy, and SOC can be inferred. Incorporating rapid impedance spectra, from which resistance and power capability can be estimated, will yield a more complete assessment of battery health. Impedance spectra measurements have gained prominence in battery research, but they had never been used for health monitoring because it has taken a long time to perform measurements and required expensive and delicate equipment in a laboratory environment. INL's rapid measurement technique has elevated this broad spectrum measurement to be incorporated into future definitions of industry standard health metrics. It can be applied before installation or during battery operation, using hardware that could be embedded. This effort supports the development of resilient control systems for energy storage applications.

Summary

A preliminary SOH assessment architecture to predict battery SOH and RUL has been formulated and implemented using the rapid impedance measurement data. The architecture includes both offline model training and online monitoring and prognostics as shown in Figure 1. The offline component uses pre-existing data to train the model's (or library of models) parameters as a function of various stress factors. The online component uses onboard sensors to acquire internal battery data such as passive measurements (voltage, current,
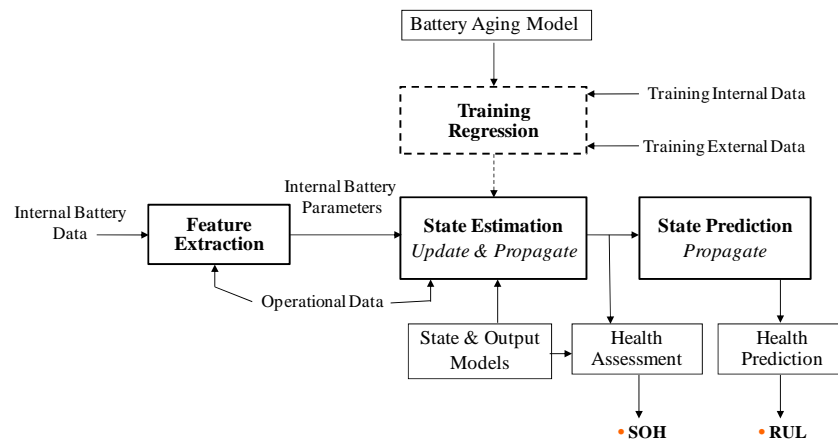

FIGURE 1. Prototype SOH and RUL assessment architecture.

temperature, etc.) and active measurements (rapid impedance measurements). These data are combined with the offline training regression for updated state estimation and state prediction. State estimations are used to develop an overall health assessment at the battery's present condition. State prediction and propagation are used to estimate remaining useful life given the health and history of battery usage. Demonstration of this preliminary SOH assessment architecture has been accomplished using some of the data acquired from previous validation studies with rapid impedance measurements under both no-load and load conditions. Since the acquired data were captured from prototype hardware and software, a data pre-processing algorithm was first developed to filter out the noisy, inconsistent, or incomplete results before applying any feature extraction tools for state estimation and prediction.

To illustrate the obtained results, Figure 2 shows a preliminary predictive estimation of battery SOH and RUL under a discharge load condition at 50°C based on a normalized health assessment (i.e., 1 is perfectly healthy, 0 is end of life). The SOH is plotted as a function of the cycle index, which corresponds to the number of shallow cycles that have been performed on the cell using a pre-defined constant power profile. The predicted SOH (red circles) result from the training regression algorithm and degradation model using the existing test data under a discharge load condition. The model can then estimate the SOH during the cycles in between measurements as shown with the green circles between cycle indexes of 0 and approximately 1.6. As shown, the model does a very good job of estimating SOH and generally lines up with the predicted results (red circles). After about 160,000 cycles, the SOH assessment architecture begins to estimate the overall remaining useful life of the cell (also shown with the green circles). For this example, the model predicts that the cell will reach end of life after approximately 230,000 cycles.
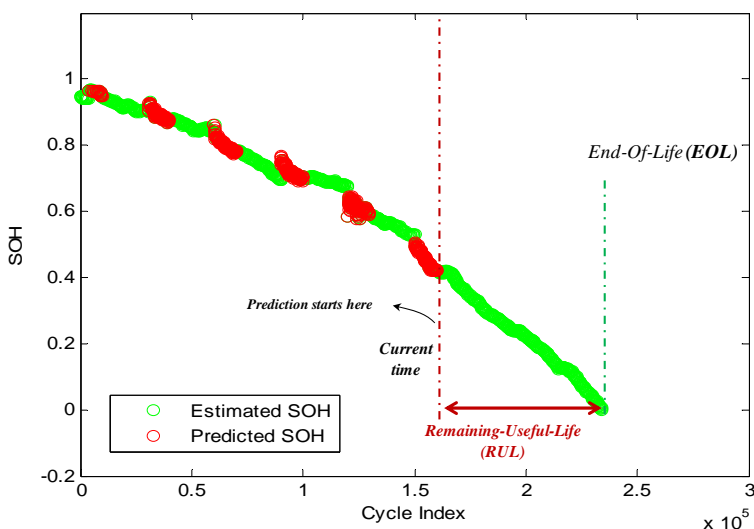
FIGURE 2. Preliminary SOH and RUL assessment using results from previous validation study.

Benefits to DOE

DOE will benefit from this research through the advancement of battery energy storage technologies, a key component of the national energy strategy. Knowledge of battery SOH and RUL is critical for optimized energy usage, control and management. Developing a more complete SOH metric will allow battery management systems to perform real-time decisions more intelligently using the developed sensor technology to better predict battery SOH and RUL.

Relevant Publications and Presentations

A peer-reviewed journal publication on the accomplishments is under preparation. Additional peer-reviewed publications are also anticipated in FY 2013 once the prototype SOH assessment architecture is further enhanced.

Christophersen, J.P., C.D. Ho, and J.L. Morrison, "Rapid Impedance Spectrum Measurement for Onboard State-of-Health Applications," *45th Power Sources Conference, Las Vegas, NV, June 11-14, 2012*.

Garcia, H.E., A. Mohanty, J.P. Christophersen, and W. Lin, "On-line State-of-Health and Remaining–Useful-Life Assessment of Batteries Using Rapid Impedance Spectrum Measurements," *45th Power Sources Conference, Las Vegas, NV, June 11-14, 2012.*

Resilient Monitoring, Adaptation, and Control (ReMAC) System

Humberto Garcia, Wen-Chiao Lin, Kris Villez,[1] and Venkat Venkatasubramanian[1]
12-082

In order to provide reliable operational management under any circumstance regarding the health and controllability of monitored processes (such as nuclear energy systems, oil refineries, electric grids, and computer networks), we are investigating resilient monitoring and control systems consisting of varying sets of multiple sensors and actuators. The objective of this research is to develop and demonstrate a rigorous framework and supporting algorithms for the implementation of condition monitoring and control systems that are both resilient and adaptive. In order to accomplish these goals, we are developing an integrated framework that uses notions of information quality (IQ) and assessment quality developed in previous projects on resilient monitoring (i.e., the ReCAM project). Notions of execution quality and control quality are also being developed in this project emphasizing resilient control for autonomous selection of not only monitoring but, more importantly, control strategies. While advancing previously developed resilient monitoring technologies (e.g., introducing the notion of learning for monitoring selection) is also one of the objectives, the primary purpose of this research is to develop resilient control selection algorithms that include control strategies of diverse degrees of complexity and adaptation that are synthesized to effectively operate on increased severity levels of plant and control conditions. Hence, a significant challenge specific to this project is assuring process stability and controllability under an environment in which not only the sensing information but also the control strategies are continually changing. With an emphasis on resilient control, high level objectives include: (1) Extending and integrating achievements within the additional development of companion methods for addressing "controllability" and "stability" challenges of these systems (based on the novel technologies introduced under the ReCAM project focusing on the monitoring aspect of resilient systems)—this objective may include the incorporation of monitoring and control technologies developed under other projects; (2) Demonstrating developed resilient monitoring and control technologies on power grid applications; and (3) Contributing to various research areas for development of resilient systems, such as physical security, cyber security, control stability and efficiency, resilient control, and state awareness dashboard.

Summary

In this project, we assume a set of sensors and actuators are used to observe and control a plant of interest, where there may be natural or malicious disturbances to the sensors, actuators, and the plant. Previously developed monitoring technologies are used to collect and interpret sensor observations for diagnosing plant health, while a supervisory controller is used to select the most appropriate controllers based on monitoring reports. Integration of these technologies results in a preliminary structure of the ReMAC system considered. At this stage of the project, the monitored and controlled plant is the INL machine condition monitoring (MCM) testbed, mimicking cooling of a chemical reactor with cold water supply and valve subsystems. Figure 1 illustrates the concept of this application.

During its first year, this project combined monitoring technologies developed in two previous projects, one lead by Purdue University and one lead by INL. In particular, monitoring technologies that work together in this project are Kalman-based diagnosis and a previously-developed ReCAM system. Kalman-based diagnosis consists of three modules: fault accommodation (FA), Kalman filter (KF), and fault detection and identification (FDI) modules. Sensor and actuator signals are first passed through FA for corrections based on previously identified faults. For example, if a bias/drift is previously identified for a particular sensor, this bias/drift is then subtracted from the sensor signal. Similarly, if a valve is previously identified as being stuck, actuator signals from the controllers to it are set 0. The corrected signals are processed by the KF and the KF prediction errors are used in the FDI to detect and identify faults in specific components of the monitored plant. The previously-developed ReCAM capability consists of three layers: information, assessment, and sensor selection layers. Based on sensor data and associated data qualities (DQs), which are part of IQ and quantifies trustworthiness of sensor data, the information layer calculates estimates of process variable probability distributions. These estimates are used in the assessment
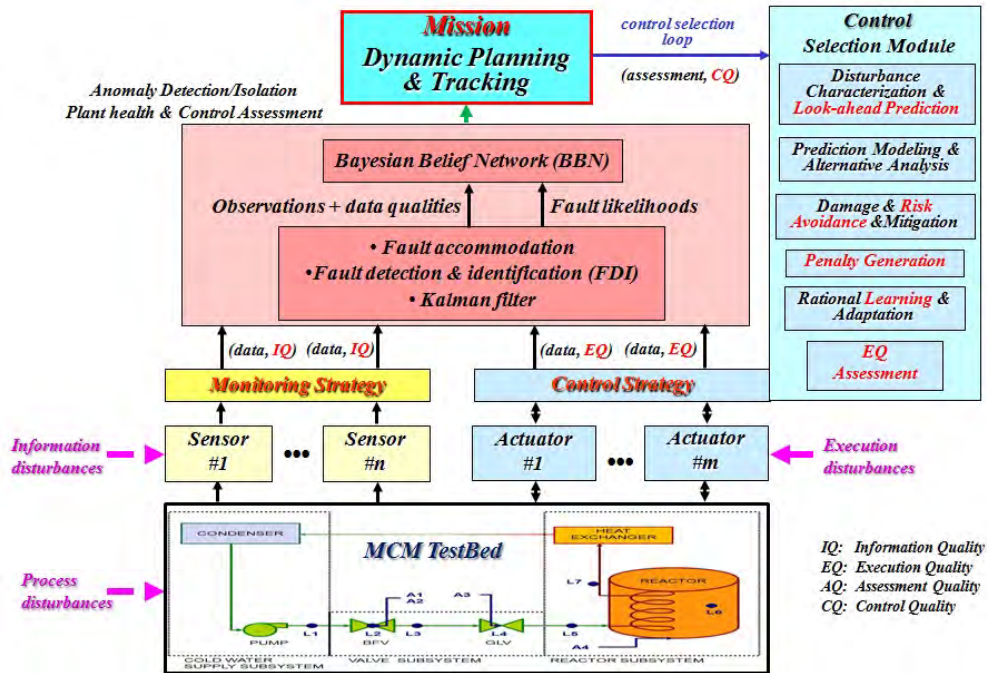
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[1] Purdue University

FIGURE 1. Application of ReMAC to MCM testbed and features of ReMAC.

layer to compute plant health estimations. This computation is based on probabilistic reasoning, and, in particular, on Bayesian belief networks (BBN). The BBN is used repeatedly with prior probabilities set as the updated plant assessments from the previous time instant. As confidence of the assessment reaches a user defined threshold, a definite decision of the plant status is made and the assessment process repeats (with prior probabilities in the BBN set to complete ignorance—i.e., uniform distributions). Based on plant health assessment calculations, sensors are then dynamically selected for monitoring performance in the sensor selection layer.

Kalman-based diagnosis focuses on detection and diagnosis of faults in plant components (e.g., a particular valve), while ReCAM focuses on computing overall plant and subsystem health. For the two monitoring technologies to work together, they are being modified. In particular, since ReCAM selects sensors dynamically, dimensions of the observations for the KF in the Kalman-based diagnosis is not fixed. In order to accommodate for this variability, matrices used in the KF as well as the KF gain are dynamically adjusted for the changes in the observation dimension. Similarly, diagnosis results from FDI indicate

the health of a specific plant component (e.g., health of a valve is normal, degrading, and blocked with certain probabilities). In order to use this information in ReCAM, the BBN in the assessment layer is modified to take this data and process it accordingly with the DQs of sensor signals used to calculate the component health.

Regulatory controllers are being designed for the MCM testbed with the goal of regulating the temperature in the reactor at desired set points. These controllers are designed offline assuming all actuators (i.e., values) are normal, some actuators are faulty, or all actuators are malfunctioning. A supervisory controller is designed to switch among these controllers based on assessed conditions of plant components or overall plant health. For example, if Kalman-based diagnosis indicates a particular valve is blocked, the supervisory controller then switches to a controller that does not use this valve (but with degraded control performance). Likewise, if ReCAM indicates the plant is down, the supervisory controller may then switch to reactor shut-down.

260

Benefits to DOE

This research is establishing scientific- and engineering-based techniques for resilient monitoring and control under natural and malicious perturbation to sensors, actuators, and physical assets. As shown throughout the project, this monitoring system is applicable to many large systems with multiple unit operations such as energy systems (e.g., chemical reactors or power plants) where a large number of sensors and actuators are deployed and may be attacked. Future work will focus on application of monitoring and protection technologies developed here to power grids, which typically span large geographical areas, providing opportunities for cyber-physical attacks on sensors and the power grid infrastructure. This project provides a path to addressing the Nation's need to prevent catastrophic consequences of such attacks and increase energy security. In general, with this project, innovations that advance the critical infrastructure systems can be discovered, developed, and deployed.

Relevant Publications and Presentations

Lin, W-C., H.E. Garcia, and K. Villez, "A Resilient Monitoring, Adaptation, and Control System for Cooling of a Chemical Reactor System," 2012. (in preparation)

Villez, K., W-C. Lin, and H.E. Garcia, "Kalman Filtering for Resilient Fault Diagnosis With Degraded Data Quality and Time-Varying Data Collection," 2012. (in preparation)

Garcia, H.E., W-C. Lin, K. Villez, and V. Venkatasubramanian, "Resilient Monitoring, Adaptation, and Control (ReMAC) System," *ICIS External Advisory Committee Review, Salt Lake City, UT, August 13, 2012.*

Garcia, H.E., et al., "Resilient Monitoring, Adaptation, and Control (ReMAC) System," *ONR/NAVSEA Workshop, Idaho Falls, ID, March 6-7, 2012.*

Garcia, H.E. and W-C. Lin, "Complexity and Graceful Degradation: ReCAM & ReMAC Systems," *Energy Security and Resilient Control Workshop*, University of Southern California, Information Sciences Institute, *Los Angeles, CA, November 2011.*

Multi-Agent Analysis to Characterize Complex Infrastructure Interdependencies

Craig Rieger, Keith Daum, Ronald Boring, Tom Baldwin, Jonathan Butts,[1] Milos Manic,[2] and John Doyle[3]
12-089

In a holistic resilient control system approach, data is fused to develop situational awareness, which provides the basis for a blended response to system degradation and operational recovery. A multi-agent design provides an adaptive, semi-autonomous mechanism for response to rapidly changing conditions with complex interdependencies. Developing a multi-agent design first requires the decomposition of the philosophy of operations (command and control) and identification of the Industrial Control System operations. This is used to codify the interdependencies and the impact to the mission. Therefore, the outcomes of the project for year one are: confirmation of Department of Defense (DoD) partners and associated characteristics to make a determination, workshop(s) to develop a list of suitable DoD candidate facilities and control system applications to use as a basis, and initial development of performance metric and communication architecture candidates.

Summary

A two-day R&D workshop on resilient energy systems was held with the University of Southern California (USC), University of Idaho, the Air Force Institute of Technology (AFIT), the University of California, Berkeley, and California Institute of Technology (Caltech). The workshop provided an opportunity to discuss ongoing research in smart grids and building energy management, as well as test beds currently in place or needed and applicable to the multi-agent project and other collaborations. These test beds included the Department of Homeland Security Science and Technology-sponsored DETER test bed. Caltech, who has been awarded Advanced Research Projects Agency-Energy Green Electricity Network Integration funding, has specific interest in using INL's simulation and real world assets for testing. AFIT is developing the partnership to focus on a smart-grid project to align with the INL multi-agent LDRD, where they are a partner, as is Caltech. A second workshop that included attendees to the 5th International Symposium on Resilient Control Systems was held based on current planned methodologies and techniques, allowing for comment by a diverse set of individuals. An outcome of this discussion was to focus on a notional Microgrid system, which is relevant to DoD and also not overly complex for the amount of funding available.

A data collection plan has been developed for targeting individuals that have an interaction with control system operation or maintenance. The plan consists of questions and multi-agent hierarchy associated with each role. The role-based data collection started from individual discussions with experts on power system operation and research. A resulting model was started by the University of Idaho that uses Fuzzy Logic and Bayesian design to codify a decomposition of this data for the Management and Coordination aspects of a Multi-agent framework (Figure 1), respectively. The University of Idaho has also developed a Microgrid Simulation, based upon other Instrumentation, Control and Intelligent Systems efforts and updated to reflect testing of the computational intelligence agents. As the multi-agent framework has a dependence on understanding optimal teaming interactions and decisions, human systems and complexity resources at the INL have provided a perspective on these aspects through a document that gives metrics guidelines for the design. Finally, the Air Force Institute of Technology has suggested a Byzantine General design for cyber security threat measures and has started research on a design associated with a notional Microgrid System.

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[1] Air Force Institute of Technology

[2] University of Idaho
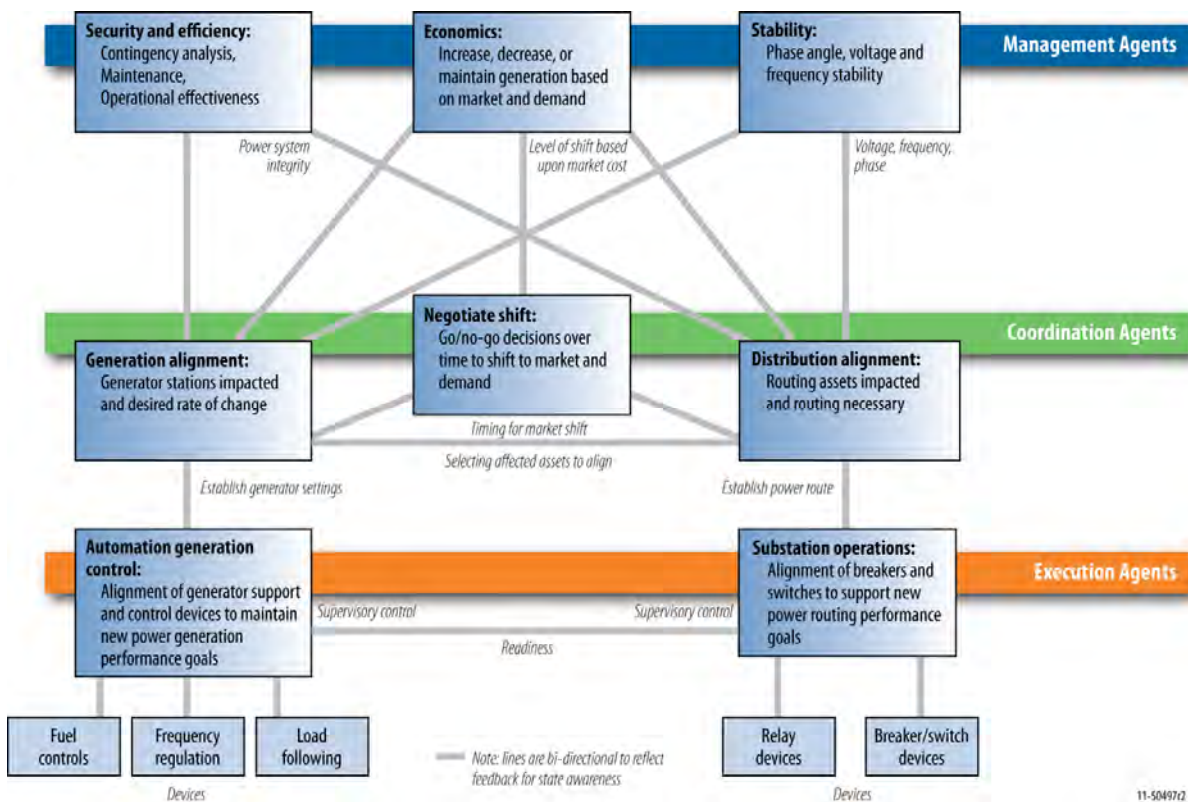
[3] California Institute of Technology

FIGURE 1. Multi-agent Framework.

Benefits to DOE

The multi-faceted nature of our energy infrastructure and the associated interdependencies will only get more complex with the implementation of digital technologies, such as designs targeted to automate the Smart Grid. While some of these advances can actually lead to more resilience, a true holistic and multi-disciplinary approach to control system design is lacking. In other words, more automation is being implemented, but the necessary modeling of the associated complexity has not been demonstrated. This research promises to provide this modeling aspect as a real world example, which can then further vet the underlying framework. In addition, cyber threat poses a new paradigm for dynamic control systems. Therefore, cyber awareness is a key component of resilient control system research, and the actions of the malicious intruder are a design factor in this effort.

Relevant Publications and Presentations

Rieger, C. and K. Villex, "Resilient Control System Execution Agent (ReCoSEA)," *ISRCS 2012, Salt Lake City, Utah, August 2012.*

Rieger, C., Q. Zhu, and T. Basar, "Agent-Based Cyber Control Strategy Design for Resilient Control Systems: Concepts, Architecture and Methodologies," *ISRCS, Salt Lake City, Utah, August 2012.*

"Energy Security and Resilient Control Systems," *Idaho National Laboratory and the University of Southern California's Information Sciences Institute, November 15–16, 2012.*

Multi-agent Session at ISRCS 2012, August 15, 2012. (invited)

"Advanced Microgrid Concepts and Technologies Workshop," *Army Research Laboratory, June 7–8, 2012.*

State Awareness for Smart Grid Electrical Load Balancing, Distribution, and Security

Victor Walker, Ronald Boring, and Timothy McJunkin
12-121

INL is developing measures and models to increase human operator and the respective automated systems' awareness of a smart-grid connected environment, and to understand the impacts of these improvements on operational performance of the grid. The emerging electrical smart grid" represents a complex environment of interconnected elements where data and inputs are driven not only by generation systems but also by consuming systems, transmission mechanisms, external sources, and consumers. In a basic sense, the smart grid is a system of systems where each element is controlled at least partly independent of other elements but with dependencies on the others for their resources and demands.

This highly complex system represents a great challenge for operators and controllers to truly gain a strong situational awareness and understand impacts of the system on declared goal states. As demonstrated by the large August 2003 power outage, and many that have followed, the increasing complexity of a Smart Grid will mandate a better human-in-the-loop characterization than is provided with current control systems.

This project's modeling, architecture, and testing will produce new and innovative ways of looking at complex systems and state awareness.

The overall tasks for this project are as follows:

- Task 1 – Defining metrics and measures for determining the levels of state awareness

- Task 2 – Inference engines/graphical models for holistic process prognosis

- Task 3 – Intelligent man-machine interface agents

- Task 4 – Dynamic human-reliability and probabilistic-risk analysis' intelligent man-machine interfaces.

Summary

As a necessary part of providing a shared cognition framework, the project focused on providing a foundational architecture for a robust and resilient control environment based on a "physiological control" design methodology, "impact definitions" as a method to define the goals of the environment and drivers of outcomes, and "operator modeling" for providing future methods to interact with the operator.

Physiological Control Architecture. Based on observations of the control systems in the human body and other natural forces, we developed an overarching control system framework that incorporates physiological design elements. This physiological architecture represents three layers of system control and feedback for increased resilience and stability, as shown in Figure 1. The lowest layer is a set of "stabilizers" and provides for localized control of resources based on immediate sensor conditions. This is designed on a negative feedback loop to always push resources to a stable state based on sensed conditions. The thresholds are tightly coupled with the feedback loop and the settings are established by the higher layers. The localized threshold monitors are intended to ensure the feedback control is stable, even in the case of any loss of communications with the higher layers of the hierarchy. At the "intention layer," sensor data and actions from the local controllers are aggregated into a state awareness picture for the impact agents. The impact agents ensure the system has adequate resources to comply with operational objectives. To do so, the system requires an accurate picture of the goal state and the current state for completing those objectives. Based on the impacts of changes to the system, the intelligent control system can provide threshold changes to the stabilizing layers to maintain objective compliance and notify the operator of impacts through the final layer (known as the "cognition layer"). The cognition layer is where the control system shapes a tailored state awareness picture for the operator response. The system maintains an understanding of the operator and the likely cognition of the operator and then provides only the information most needed based upon operational priorities and the impacts of the system state on the goals. This interaction allows the operator to be more focused, and to adaptively adjust the control system to emergent events.
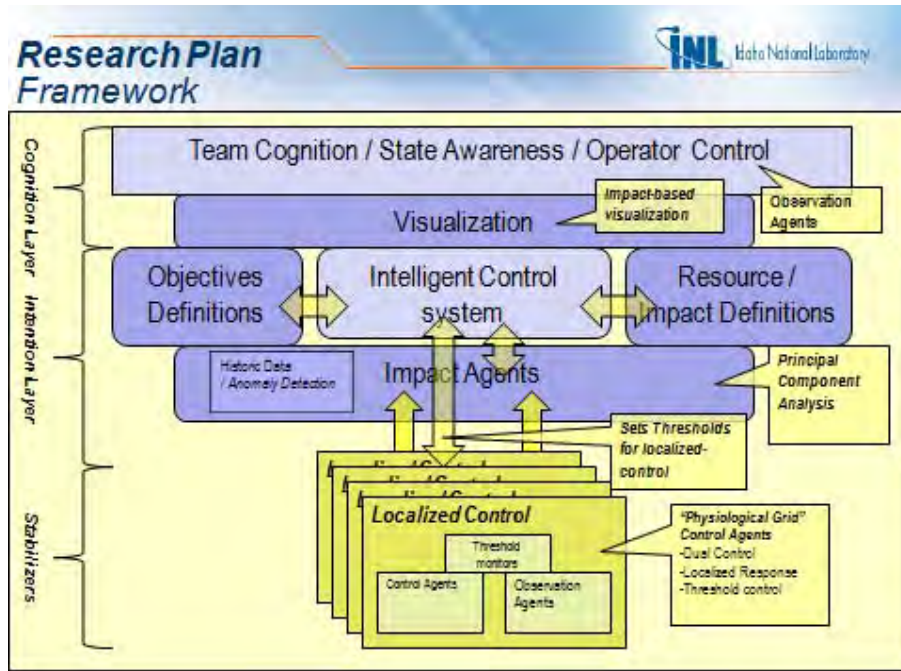
FIGURE 1. Physiological Architecture.

Impact Definitions. To truly impact situational awareness and enhance decision making, this project attempts to provide not only state information, but also the anticipated impacts the state of the system has on the goals of the system. This will allow for operators and intelligent controls to focus on what the most significant events are and what potential actions should be taken to best maintain system performance.

To properly identify the impacts, both the system and the operator need to understand the current goals of the system and what resources are available to meet these goals. We are developing a generic language and representation for defining and communicating these elements and resources. In addition, we are studying the methods for representing state changes to describe potential actions and how the process to meet the goal state can best be reported.

Operator Modeling. As part of improving team cognition it is essential for both the operator and the system to have an accurate model of each other. Studies traditionally focus on the awareness of the operator's cognition of the system

state. To accomplish this joint-cognition model, we are developing a representation of the operator and the operator's focus. This will help the system present relevant information in the most effective way and increase the shared understanding and cognition with the operator.

Benefits to DOE

This project will benefit DOE in providing ways to deal with large volumes of cyber-physical data that must be consumed and interpreted for implementation of the Smart Grid. All realistic control systems will have a human in the control loop. However, operators are routinely overloaded with data and conflicting objectives that lead to power outages and other cascading failures. This project intends to develop next-generation cyber-physical visualizations and improved situational awareness processes that can have application to many energy domains and operational control systems.

Relevant Publications and Presentations

Walker, V., *ICIS External Advisory Committee Review, Salt Lake City, UT, August 13, 2012.*

APPENDICES

Appendix A

Commonly Used Acronyms

The following acronyms are used in many of the project descriptions.

ATR	Advanced Test Reactor
BIGHORN	Neutronic Solver for Prismatic Geometry Computer Code
CAES	Center for Advanced Energy Studies
CAVE^{TM}	Computer Assisted Virtual Environment
CAMS	Center for Advanced Modeling and Simulation
CRADA	Cooperative Research and Development Agreement
DOE-NE	Department of Energy Office of Nuclear Energy
INL	Idaho National Laboratory
IRC	Idaho National Laboratory Research Center
LDRD	Laboratory Directed Research and Development
MARMOT	Mesoscale Model Application Computer Code
MFC	Materials and Fuels Complex
MOOSE	Multiphysics Object Oriented Simulation Environment
NSUF	National Scientific User Facility
PI	Principal Investigator
R&D	Research and Development

Appendix B

Relevance to Major National Programs

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
07-052	Scott, Jill	Laser-Induced Breakdown Spectroscopy: Development and Application of In Situ Elemental Analysis for Process Streams in Spent Fuel Reprocessing Facilities		P					S				
09-068	Jue, Jan-Fong	On-line Monitoring of Actinide Concentrations for Advanced Aqueous Separation Processes	P					S					
10-001	Mincher, Bruce	Neptunium Redox Chemistry in Irradiated Aqueous Nitric Acid			S			P					
10-007	Taylor, Steven	Ultrasonic Transducer Sensors for In-Pile Detection of Dimensional Changes	S					P	S				
10-008	Millet, Paul	Irradiation-Induced Evolution of Defects and Microstructures in Nanocrystalline BCC Mo					S	P					
10-011	Apel, William	Degradation and Conversion of Lignin Using Extremophilic Systems		P			S						
10-014	Shunn, Lee	Automated Differential Equation-Based Identification	S	S			P	S					
10-015	Simpson, Michael	Optimization of Ceramic Waste Forms Used for Electrochemical Processing of Spent Nuclear Fuel						P					
10-017	Williamson, Richard	Multiscale Modeling and Simulation of Nuclear Fuel Performance					S	P					
10-022	Gan, Jian	In-Pile Temperature Monitor and Control for ATR						P					
10-023	Rabiti, Cristian	Study of Preconditioning Techniques for Krylov Solvers Applied to Hybrid Neutron Transport Calculations						P					
10-024	Sencer, Bulent	Small Specimen Test Techniques for Evaluating Radiation-Induced Changes in Mechanical Properties						P					
10-026	Herbst, Scott	Reversible Gas Phase Reactions for Recovery of Graphite from Recycled HTGR TRISO Fuel		S				P					
10-027	Zalupski, Peter	Comprehensive Thermodynamic Models for Aqueous Partitioning of Actinides from Used Nuclear Fuel	S		S		S	P		S			S
10-029	McKay, Mark	3-D Spatial Representation in Support of Design Inspection and Verification	P					S					
10-031	Yu, Jianguo	Fickian and Thermal Diffusion in Nuclear Materials from Linear Response Theory and Multiscale Simulations					S	P		S			

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
10-032	Lister, Tedd	Investigation of Molten Bromide Salt Systems for Separation and Recovery of Actinides from Fission Products			S			P		S			
10-037	Garcia, Humberto	Resilient Condition Assessment Monitoring (ReCAM) System	S	P		S	S	S			S	S	
10-053	McLing, Travis	Prediction and Monitoring of CO_2 Behavior in Deep Reactive Geologic Formations				P					S	S	
10-056	Cole, James	Fabrication of Advanced ODS Alloys Using Field-Assisted Sintering					S	P					
10-058	Okuniewski, Maria	Microstructural Evolution of UO_2 and U Under Irradiation						P	S				
10-059	Garcia, Humberto	Feedstock Processing and Energy Storage		P		S		S			S		
10-060	Janney, Dawn	Spatially-Correlated Microstructural Characterization: from Centimeters to Nanometers	S		S		S	P		S			S
10-064	Richins, Bill	Multi-Rate Shock Physics Simulation of Blast and Penetration Events in Concrete	S				S	P		S			
10-065	Jeffers, Robert	Water and Energy System Interdependency Modeling for Multicriteria Decision Analysis		P	S	S	S	S			S		
10-067	Cherry, Robert	Hybrid Systems Process Integration and Dynamics Studies		S		S		P					
10-068	Sencer, Bulent	Irradiation Testing and Molecular Modeling of Irradiation-Assisted Diffusion and Microstructural Evolution (FCCI)						P					
10-073	Roybal, Lyle	Next Generation Control System "Smart Grid" Simulation Environment		S							P		
10-075	Moradi, Hussein	Wireless Communications R&D	S				S	S		P			
10-078	Newby, Deborah	Development of Non-Lethal Methods for Enhanced Lipid Recovery from Microalgae		P			S						
10-079	Joe, Jeffrey	Transmission Site Suitability Decision Support Technology		S	S		S				P		
10-080	Searcy, Erin	Design and Operational Improvements, and LCA in Anaerobic Digestion of Fermented Dairy Manure Using a Two-Stage Process		P	S								
10-081	O'Brien, James	Design and Testing of a Mars Hopper					S	P					
10-083	Teysseyre, Sebastian	In Situ Characterization of an Oxide Film for Prediction of Stress Corrosion Cracking Susceptibility					S	P					

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
10-087	Apel, William	Biological Fixation of CO_2 for Fuel and Chemical Production Using Acetogen Intermediary Metabolism		P			S						
10-088	Myers, Kurt	CAES Vertical Axis Wind Turbine		P									
10-092	Stewart, Frederick	Hybrid Osmosis Water Purification Systems Research		P	S	S		S					
10-093	Zhao, Haihua	Nuclear Reactor Safety Case					S	P	S				
10-094	Whiting, Eric	Advanced Visualization Using Immersive Environments	S	S	S	S	S	P			S		
11-000	Crawford, Anthony	Haptic Tele-Operated End Effector for Hazardous Environments	S		S			P	S	S		S	
11-005	Riddle, Catherine	Speciation Behavior of Americium Oxidation States for the Separation of Americium from Curium in Nuclear Processing		S				P					
11-006	Mincher, Bruce	Supercritical Fluid Extraction of Actinides from TRISO Reactor Fuels			S			P		S			
11-007	Baldwin, Thomas	Integration of Renewable Energy Resources Through Energy Storage and SuperGrid		P							S		
11-019	Lister, Tedd	Electrochemical Production of Synthesis Gas from CO_2		P									
11-022	Welker, Kurt	Electronic Warfare Digital Communications and Network Traffic Modeling						P					
11-023	Martin, Leigh	Development of a Simplified Soft Donor Technique for Trivalent Lanthanide Actinide Separations			S		S	P		S			S
11-031	Ginosar, Daniel	Mechanisms of Self Inhibition of Catalytic Conversion of CO_2 to Methanol		P		S	S						
11-037	Schley, Robert	Development of In-Reactor Experiment Configuration for Laser Based Material Properties Measurement						P					
11-041	Khafizov, Marat	In Situ Micro-Raman Spectroscopy and Modeling of Breakaway Oxidation of Zircaloy Cladding	S	S	S		S	P	S	S		S	
11-042	McQueen, Miles	Experimental Cyber Security Vulnerability Prediction, Discovery, and Mitigation					S	S			P		
11-043	Jackson, John	Characterization of Nanomechanical Response of Material to Determine Key Variables in Stress Corrosion Cracking					S	P	S				

Appendix B **B-3**

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
11-045	Huang, Hai	Multiscale Coupled Hydrogeophysics Modeling: Advancing Understanding of Reactive Transport and Effective Subsurface Environmental Monitoring			P	S	S						
11-046	McQueen, Miles	Known Secure Sensor Measurements for Detecting Unauthorized Process Manipulation and Falsification of State					S	S			P		
11-051	Lessing, Paul	Alternative Processing for Improved UO$_2$-Based Fuels						P					
11-055	Akers, Douglas	Spatially Resolved Positron Analysis of Hydride Formation in LWR Fuels with GE - Global Nuclear Fuels						P		S			
11-059	Chichester, David	Unconventional Radiation Detection Methods for Nuclear Nonproliferation, Safeguards, and Treaty Verification	P				S	S					
11-060	Chu, Henry	SMC Advanced Armor Materials and Systems R&D and D&D	S				P	S					
11-061	Martineau, Richard	Advanced Modeling and Simulation Concepts for ATR						P	S				
11-062	Hugo, Jacques	Full-Scope Human System Simulation Laboratory for Plant-Specific and Generic NPP Simulator Models Studies					S	P					
11-064	Alessi, Sam	Dynamic Thermo-Mechanical Energy Conversion Simulation		P			S				S		
11-065	Gertman, David	Development and Demonstration for National Fuel Efficiency		S		S						P	
11-066	Rieger, Craig	Targeted Energy Management Toolset for Comfort and Savings Based on Advanced Computational Intelligence Techniques		P		S					S		
11-069	Gasper, Peter	Industrial Control System Threat Axis Analysis to Characterize and Quantify Malicious Intent from a Threat Actor	S								P		
11-074	Pernice, Michael	Uncertainty Analysis for Multiscale Models of Nuclear Fuel Performance	S		S	S	S	P					
11-075	Pernice, Michael	Uncertainty Analysis for Mesoscale Models of Radiation Effects in Materials	S				S	P	S				
11-076	Mandelli, Diego	Exploratory Nuclear Reactor Safety Analysis and Visualization via Integrated Topological and Geometric Techniques	S				S	S	P				
11-077	Hruska, Ryan	Prototype INL Wildland Fire Early Warning and Situational Awareness System			S		S	P				S	

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
11-078	Deaton, Juan	Enabling Dynamic Spectrum Access in Long Term Evolution Networks	S	S							P		
12-001	Derr, Kurt	Long Term Evolution Wireless Cyber Security	S				P	S			S		
12-007	Youngblood, Robert	Uncertainty Quantification of Safety Codes Using a Bayesian Approach with Data from Separate- and Integral-Effects Tests						P	S				
12-013	Klaehn, John	Olefin Gas Separations Using Embedded Transition Metal Chelates in Polymeric Membranes		S	S	P		S					
12-017	Langhorst, Benjamin	Polymer Components in Laminate Armor Systems for Ballistic Protection										P	
12-026	Xianming, Bai	Protectiveness and Stability of the Zirconium Oxide in Early-Phase Corrosion of Zirconium Alloys: Predictive Relations to Surface Structure and Composition					S	P					
12-031	Teague, Melissa	2-D and 3-D EBSD Technique Development and Microstructure Reconstruction for Phase Field Microstructure Evolution Models						P		S			
12-043	Boring, Ronald	Science-Based Simulation Model of Human Performance for Human Reliability Analysis						P	S				
12-045	Sabharwall, Piyush	Development of an Uncertainty Quantification Method for MIR Facility		S	S	S	S	P					S
12-046	Thompson, Vicki	A Novel Bioreactor to Study the Human Microbiome						S					
12-049	Gerts, David	Coupled Neutral to Charged Particle Transport Algorithms and Detectors	P					S	S				
12-050	Clement, Ryan	Cross Section Representations for Nuclear Nonproliferation	P					S	S				
12-051	Apel, William	Thermo- and Acid-Stable Enzymes for Improved Animal Feed Nutrient Digestion		S	S			P					
12-054	Kinlaw, Mathew	Treaty Verification with Photo-Induced Prompt Signatures	P										
12-056	Zalupski, Peter	Recovery of Precious Metals from Used Nuclear Fuel and Electronic Waste Using Sulfur-Impregnated Nanoscaffolds			S			P					
12-059	Herbst, Scott	Chemistry and Flowsheet Development for Lanthanide Separations		S	S	S	S	P	S				
12-061	Mariani, Robert	Development of a High Burnup Zr-Based Fuel Cladding for LWRs					S	P					

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
12-062	Chichester, David	Development of Diamond-Based Sensors for User Facility Capabilities at INL Advanced Test Reactor	S				S	P	S				
12-066	Daniels, Michael	Electronic Energetic Initiation						P					
12-069	Wharton, Jayson	Fast Identification of Chemical Warfare Agents, Explosives, and Radionuclides with Lanthanum Bromide Gamma-Ray Detectors	P					S					
12-070	Jewell, Keith	Separate Effects Fuels Development Capability	S	S			S	P					
12-071	Christophersen, Jon	Battery Resilient Monitoring and Control		P							S	S	
12-073	Thompson, Scott	A Nonproliferation-Focused Study and Comparison of the GEANT4 Simulation Toolkit and MCNP Functionality, Accuracy, and Development Needs	P										
12-077	Khafizov, Marat	Observation of Zirconium Oxidation at Atomic Level Using Nonlinear Optical Spectroscopy					S	P					
12-080	Khafizov, Marat	Characterization of Intergranular Corrosion Using Thermal Wave Imaging					S	P					
12-081	Scott, Jill	Demonstration of Total Ion Control (TIC) Technology	S	P	S	S	S	S				S	
12-082	Garcia, Humberto	Resilient Monitoring, Adaptation, and Control (ReMAC) System	S	P		S	S	S			S	S	
12-086	Boring, Ronald	Alert/Alarm Dashboard					S	P			S		
12-089	Rieger, Craig	Multi-Agent Analysis to Characterize Complex Infrastructure Interdependencies	S	S			P	S			S		
12-090	Stoots, Carl	Development of Emissivity-Tuned, Robust Encapsulated Radioisotope Heat Sources for NASA's New Advanced Radioisotope Thermo-Photovoltaic Power System					S	P					
12-092	Clement, Ryan	Multi-Modal Radiation Detection for Nuclear Nonproliferation and Treaty Verification	P				S	S					
12-093	Fox, Robert	Development of Unique Nanomaterials for Selective Replacement of Strategic and Critical Materials		P			S						
12-094	Anderson, Matthew	Unmanned Aerial Vehicle-Based Remote Sensing and Data Fusion for Energy and Environmental Applications	S	S	P	S	S	S					S
12-096	Wilson, Aaron	Isolation and Purification of Critical Metals Using Ionic Liquid-Based Solvent Extraction		P	S			S					

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
12-099	Henriksen, James	Designing Algal Biofuel Consortia for Increased Function and Reduced Nutrient Costs		P			S						
12-100	Guillen, Donna Post	Multiphase Flow Modeling Capability for Waste-to-Energy Process Development		P									
12-101	Lee, Randy	Development of Full-Waveform LiDAR Capabilities for Water Resources and Vegetation Monitoring		S	P		S	S			S		S
12-105	Ankeny, Mark	Lower Boise River Water Quality and Natural Resources Management		P	S		S	S					
12-107	Roberto, Frank	Targeted Elimination of Pharmaceutical Compounds from Municipal Wastewater Effluent and Solids		P	S		S					S	
12-108	Wood, Thomas	Bakken Hydraulic Fracturing Water Needs and Potential Impacts to the Fox Hills/Hell Creek Aquifer: A Spatial-Temporal Approach			S	P	S					S	
12-111	Koudelka, John	Understanding the Importance of the Role of Soil Moisture Effects for Estimating Snowmelt Runoff in a Mountainous, Snowmelt-Driven Watershed		S	P	S	S	S				S	S
12-112	Carroll, Mark	Reactor Coolant Pump Alternate Can Material Development Program	S	S				P	S		S		
12-113	Lu, Chuan	Coupled Smoothed Particle Hydrodynamics and Discrete Element Model (SPH-DEM) Simulations of Hydraulic Fracturing and Shale Gas Production			S	P	S			S		S	
12-116	Clark, Denis	Monitoring and Control of the Hybrid Laser-GMAW Process		S				P`					
12-117	Gougar, Hans	Feasibility of a Broad Application Test Reactor Using LEU		S				P					
12-118	Harrup, Mason	A Leap Ahead in Energy Storage: An Integrated Approach to an Inorganic High Energy Lithium Battery		P							S		
12-120	Yu, Jianguo	Modeling-Guided Development of Nanostructured High Energy Electrode Materials for Li-Ion Batteries		P			S						
12-121	Walker, Victor	State Awareness for Smart Grid Electrical Load Balancing, Distribution, and Security						S			P		

Tracking No.	PI Name	Title	NNSA	EE	EM	FE	SC	NE	NR	OCRWM	OE	ESH	LM
12-124	Bragg-Sitton, Shannon	Model Development for Transient Performance Analysis of a Small Modular Reactor in a Hybrid Energy System		S		S		P			S		
12-129	Bragg-Sitton, Shannon	Nuclear Hybrid Energy Systems Reactor Subsystem Modeling and Infrastructure Development for Integrated Hardware Testing						P					

Appendix C

Author Index