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Laboratory Directed Research and Development (LDRD)

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ACRONYMS

3S	Safety, Security, and Safeguards
3SBD	Safety, Security, and Safeguards by Design
AC	alternating current
AD	anaerobic digestion
ADMCS	AKUFVE dynamic mixer/centrifugal separator
AEM	Advanced Electrolyte Model
AKUFVE	apparatus for continuous measurement of distribution factors in solvent extraction (translation of Swedish abbreviation to English)
ANI	active neutron interrogation
ARTIST	Advanced Reactor Technology Integral System Test
ATF	accident-tolerant fuel
ATR	Advanced Test Reactor
BMS	battery management system
CAES	Center for Advanced Energy Studies
CAN	controller area network
CF	catastrophic failure
CFD	computational fluid dynamics
CFEM	continuous finite element method
CHF	critical heat flux
CHP	1-cyclohexylpiperidine
CMPO	N,N-(diisobutylcarbamoyl)methyl,octyl,phenyl phosphine oxide
CNT	carbon nanotube
CV	cyclic voltammetry
DCPD	direct-current potential drop
DEM	discrete element method
DER	distributed energy resource
DFM	drift-flux model
DFT	density functional theory
DHS	Department of Homeland Security
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOE-EERE	U.S. Department of Energy Office of Energy Efficiency and Renewable Energy
DOE-FE	U.S. Department of Energy Office of Fossil Energy
DOE-NE	U.S. Department of Energy Office of Nuclear Energy
DOE-OE	U.S. Department of Energy Office of Electricity
DOE-SC	U.S. Department of Energy Office of Science

DSA	dynamic spectrum access
DTF	density functional theory or distributed test facility
EDF	electric-drive vehicle
EDTA	ethylenediaminetetraacetic acid
EGS	enhanced geothermal system
EIS	electrochemical impedance spectroscopy
EMF	1-ethyl-3-methylimidazolium fluorohydrogenate
ESD	electrostatic discharge
ESI	electrospray ionization
ESRP	eastern Snake River Plain
ESS	energy storage system
EXAFS	extended x-ray fine structure
FIB	focused-ion beam
FIRES	Firebrick Resistance-Heated Energy Storage
FMI	Functional Mockup Interface
FO	forward osmosis
FOD	β-diketone 1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione
FY	fiscal year
GB	grain boundary
GFDM	generalized frequency division multiplexing
GIC	geomagnetic-induced current
GIC	ground-induced current
GMD	geomagnetic disturbance
GPS	Global Positioning System
HES	hybrid energy system
HF	high frequency
HHT	Hilber-Hughes-Taylor
HIL	hardware in the loop
HTTL	High-Temperature Test Laboratory
HUM	highly enriched uranium
I/O	input/output
ICS	industrial control system
IHX	intermediate heat exchanger
INL	Idaho National Laboratory
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LDRD	laboratory-directed research and development
LN	lanthanide

LNMO	lithium nickel manganese oxide
LOCA	loss-of-coolant accident
LOD	limit of detection
LTE	Long-Term Evolution
LWR	light-water reactor
M&S	modeling and simulation
MA	minor actinide
MAC	medium access control
MBM	MOOSE-BISON-MARMOT
MD	molecular dynamics
MISCO	modeling, integration, simulation, controls, and optimization
MIT	Massachusetts Institute of Technology
MITR	Massachusetts Institute of Technology Research Reactor
MNP	magnetic nanoparticles
MS	mass spectrometry
NDE	nondestructive evaluation
NEAMS	Nuclear Engineering Advanced Modeling and Simulation
NHES	nuclear hybrid energy system
NNSA	National Nuclear Security Administration
NREL	National Renewable Energy Laboratory
NROSS	nuclear renewable oil shale system
NTE	neutron transport equation
NUC	National University Consortium
OFA	other funding agency
OECD	Organization for Economic Cooperation and Development
OFDM	orthogonal frequency division multiplexing
OSU	Ohio State University
PA	phosphoranimine
PB-FHR	pebble-bed, fluoride-salt-cooled, high-temperature reactor
PCHE	printed circuit heat exchanger
PFC	phase field crystal
PHA	polyhydroxyalkanoates
PLC	programmable logic controller
PRA	probabilistic risk analysis
R&D	research and development
RASA	Radionuclide Aerosol Sampler/Analyzer
RTD	radiative neutron equation

RTDS	Real-Time Digital Simulator
RTPS	Real-Time Process Simulator
SAAF	self-adjoint angular flux
SBLT	Spline-Based Table-Look-up
SCgPC	Stochastic Collocation generalized Polynomial Chaos
SD	self discharge
SDR	software-defined radio
SEI	solid electrolyte interphase
EM	scanning electron microscopy
SMM	surface-modified material
SNM	special nuclear material
SPS	spark plasma sintering or switchable polarity solvent
SX	solvent extraction
TAC	thermoacoustics
TAP	temporal analysis of product
TEM	transmission electron microscopy
TREAT	Transient Reactor Test
TWERL	TREAT Water Environment Recirculating Loop
UI	University of Idaho
UN	uranium mononitride
UNM	University of New Mexico
UV/Vis	ultraviolet/visible
VFA	volatile fatty acid
WNUF	Wireless National User Facility
XFEM	extended finite element method
XPS	x-ray photon spectroscopy
XRD	x-ray diffraction

INTRODUCTION

The Laboratory Directed Research and Development (LDRD) Program at Idaho National Laboratory (INL) reports its status to the U.S. Department of Energy (DOE) by March of each year. The program operates under the authority of DOE Order 413.2B, "Laboratory Directed Research and Development" (April 19, 2006), which establishes DOE's requirements for the program while providing the laboratory director broad flexibility for program implementation. LDRD funds are obtained through a charge to all INL programs. This report includes summaries of all INL LDRD research activities supported during Fiscal Year (FY) 2015.

INL is the lead laboratory for the DOE Office of Nuclear Energy. The INL mission is to discover, demonstrate, and secure innovative nuclear energy solutions, other clean energy options, and critical infrastructure with a vision to change the world's energy future and secure our critical infrastructure. Operating since 1949, INL is the nation's leading research, development, and demonstration center for nuclear energy, including nuclear nonproliferation and physical and cyber-based protection of energy systems and critical infrastructure, as well as integrated energy systems research, development, demonstration, and deployment. INL is managed and operated by Battelle Energy Alliance, LLC, a wholly-owned company of Battelle, for the DOE since 2005. Battelle Energy Alliance, LLC, is a partnership of Battelle, BWX Technologies, Inc., AECOM, the Electric Power Research Institute, the National University Consortium (Massachusetts Institute of Technology, Ohio State University, North Carolina State University, University of New Mexico, and Oregon State University), and the Idaho University Collaborators (University of Idaho, Idaho State University, and Boise State University).

Since its creation, INL's research and development (R&D) portfolio has broadened with targeted programs supporting national missions to advance nuclear energy, enable clean energy deployment, and secure and modernize critical infrastructure. INL's research, development, and demonstration capabilities, its resources, and its unique geography enable the integration of scientific discovery, innovation, engineering, operations, and controls into complex large-scale testbeds for discovery, innovation, and demonstration of transformational clean energy and security concepts. These attributes strengthen INL's leadership as a demonstration laboratory. As a national resource, INL also applies its capabilities and skills to specific needs of other federal agencies and customers through the DOE's Strategic Partnership Program.

LDRD is a relatively small but vital DOE program that allows INL, as well as other DOE laboratories, to select a limited number of R&D projects for the purposes of:

- Maintaining the scientific and technical vitality of INL
- Enhancing INL's ability to address future DOE missions
- Fostering creativity and stimulating exploration of forefront science and technology
- Serving as a proving ground for new research
- Supporting high-risk, potentially high-value R&D.

Through LDRD, INL is able to improve its distinctive capabilities and enhance its ability to conduct cutting-edge R&D for its DOE and Strategic Partnership Program sponsors.

LDRD Selection Process

Each year, projects are selected for inclusion in the LDRD Program through a proposal process. To select the best and most strategic of the ideas submitted, the associate laboratory directors responsible for the various mission areas establish committees for the focus area to review new proposals and associated ongoing projects. The committees are staffed by senior research and technical managers who are subject matter experts and have no conflict of interest regarding the proposed projects.

Proposals for project funding for both the Strategic Initiatives R&D Fund and University Partnership Fund undergo two rounds of review. In the first round, the committees evaluate short preliminary proposals and select the most promising for development into full proposals. In the second round, the committees review the full proposals, as well as ongoing projects that are requesting second- or third-year funding. After the reviews are completed, the committees provide funding recommendations to the associate laboratory directors, who in turn present the recommendations along with their input to the deputy director for Science and Technology, who develops an overall funding strategy and provides approvals for the investment. All projects selected for funding must also receive concurrence from the DOE Idaho Operations Office.

LDRD Investment Focus Areas

In FY 2015, $17.56M was allocated to the INL LDRD Program (Figure 1). This funding supported 81 projects, 29 of which were new starts (Figure 2).

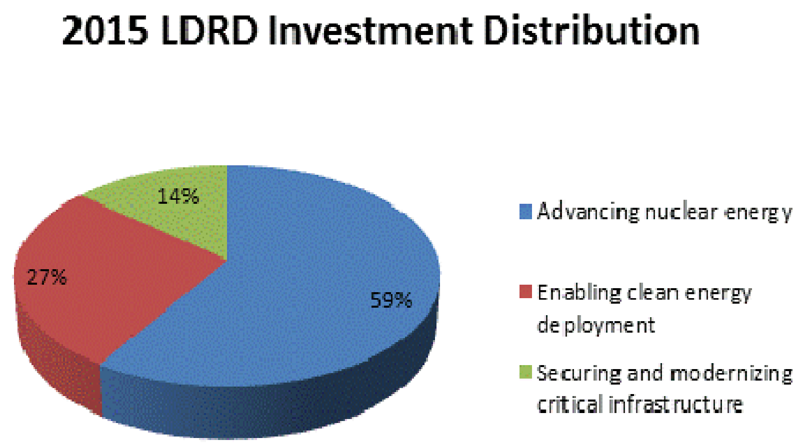

Figure 1. Level of LDRD fund investment by INL mission focus area for FY 2015.

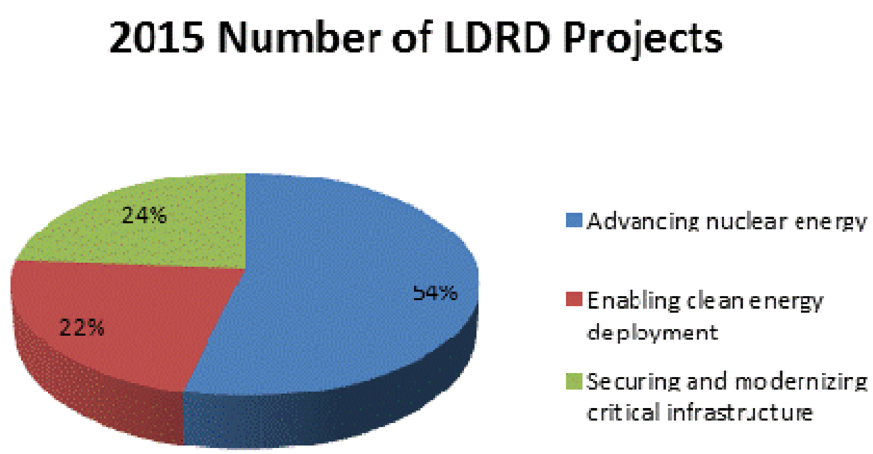

Figure 2. LDRD projects by INL mission focus area for FY 2015.

To meet the LDRD objectives and fulfill the particular needs of INL, a Strategic Initiatives R&D Fund and a University Partnership Fund were established (Table 1). The Strategic Initiatives R&D Fund helps develop new capabilities in support of INL strategic objectives. The University Partnership Fund helps build and sustain university collaboration.

Table 1. Overview of the Strategic Initiative R&D and University Partnership funds.

	Strategic Initiatives R&D Fund	University Partnership Fund (NUC, CAES)
Purpose	Address research priorities of the INL mission areas	Help build university collaboration while addressing research priorities of INL
Reviewers	Mission directorate review committees composed of senior technical managers and subject matter experts	Partnership-led review committees composed of senior technical managers and subject matter experts
Review process	Preliminary and full proposal review, which may include a presentation to the review committee	Preliminary and full proposal review, including a presentation to the review committee
Review cycle	Annual	Annual
Avg. project budget	Typically ~$220K/year	Typically ~$251K/year
Project duration	12–36 months	12–36 months
LDRD outlay	$15.42M (87% of program)	$2.366M (13% of program)

CAES = Center for Advanced Energy Studies
NUC = National Universities Consortium

The Strategic Initiatives R&D Fund is the strategic component of the INL LDRD Program and the key tool for addressing the R&D needs of the INL mission priority areas. The University Partnership R&D Fund is the key tool for building and promoting university collaboration and support of R&D needs in the INL mission priority areas. The initiatives, which are the focus of the INL strategy, are the critical areas on which INL must concentrate if it is to be prepared to meet future DOE and national requirements for nuclear energy.

The success of some of the strategy depends to a large extent on INL's ability to identify and nurture cutting-edge science and technology on which enduring capabilities can be built; these are called focus areas. INL uses the resources of the Strategic Initiatives R&D and University Partnership funds to encourage the research staff to submit proposals aimed at addressing mission focus area research goals. Each spring, the mission directors issue calls for proposals (one call for each mission area, and one call each for building National University Consortium and Center for Advanced Energy Studies partnership). The call emphasizes specific research priorities that are critical to accomplishing INL's strategic mission areas; described below are FY 2015 priorities. For the sake of simplicity in this report, each LDRD project has been assigned to a single mission focus area, though most LDRD projects have applicability to developing capabilities and unique scientific results that support multiple mission areas (see the appendix to this report for project relevance to various agencies and DOE offices).

Advancing Nuclear Energy

During the FY 2015, INL invested $8.94M in 44 LDRD projects in support of Advancing Nuclear Energy mission areas, as follows:

- *Reactor Analysis, Safety, and Simulation.* The objective of this investment is to ensure safe, reliable, and economical performance of existing nuclear power plants and to enable rapid deployment of advanced systems. Research areas included new reactor concepts, as well as enhancements to existing concepts and designs, adaptation to power grid dynamics, load following, hybrid energy systems, and new approaches to dealing with the various sources of investment risk, and other potential risk-reducing strategies. Research was also conducted to address the safety of reactors in the context created by the Fukushima accident. This research included ideas that can provide and demonstrate a quantifiable enhanced response of the overall systems to accident situations, as well as new ideas that demonstrate enhanced pre- and post-accident management. In FY 2015, INL invested $2.05M in six projects in this area.

- *Fuel Cycle Separations*. The objective of this investment is development of new laboratory-scale separations R&D capabilities or results that will support advancing nuclear energy mission areas and key strategic outcomes. LDRD investments focused on projects that developed capabilities at INL that could lead to eventual research or process demonstration with highly radioactive materials in the Remote Analytical Laboratory at the Idaho Nuclear Technology and Engineering Center (over the next 2–5 years). In FY 2015, INL invested $1.51M in six such LDRD projects.
- *Fuels and Materials R&D.* The objective of this investment is to advance basic development in the areas of (a) advanced fuel fabrication techniques for metal fuels, ceramic fuels, and composite fuels; (b) advanced measurement techniques to characterize fresh and irradiated fuels at the microstructural level; (c) online instrumentation for in-pile experiments; (d) innovative ideas for out-of-pile testing of fuels and materials for targeted phenomenology; (e) innovative ideas for analyzing the post-irradiation examination data; and (f) innovations in coated-particle fuel. More specifically, the investments focused on research that coupled experimental studies with multiscale, multiphysics modeling methods. In FY 2015, INL invested $4.41M in a total of 17 LDRD projects in this area.
- *Advancing User Facility Capabilities.* The objective of this investment is the development of advanced instrumentation for both in- and out-of-reactor fuels and materials performance, as well as innovative post-irradiation examination capabilities that address challenges associated with testing of large numbers of highly irradiated samples. In FY 2015, INL invested $1.07M in a total of four such projects in order to enhance instrumentation techniques available to users conducting irradiation tests and post-irradiation examination.
- *Used Fuel Disposition:* The objective of this investment is the analysis of storage and safe management of used fuel, specifically with regard to the validation of INL tools based on experimental data. The focus was development of methodologies and tools that would facilitate verification, validation, uncertainty quantification, and scaling analyses. In FY 2015, INL invested $0.74M in two LDRD projects in this area.
- *Nuclear Nonproliferation.* The objective of this investment is to focus on building INL's ability to forecast potential nuclear proliferation risks to help propose and implement U.S. programs that can deter further nuclear weapons development. The emphasis of this research is on (a) safeguards/ nonproliferation/forensics-focused nondestructive assay measurements of irradiated fuels within the nuclear fuel cycle; (b) advanced gamma-ray spectrometry in support of nonproliferation programs; (c) evaluation and demonstration of the integration of safeguards, safety, and security concepts; (d) advancement of nuclear cyber-physical security systems; (e) advancement of capabilities at the Nuclear and Radiological Activity Center to detect and characterize special nuclear materials; (f) advancement of mass spectrometric analysis techniques for signature identification or detection; and (g) advancement of particle dispersion and transport for emergency response. In FY 2015, INL invested $0.84M in 10 LDRD projects in this area.

Enabling Clean Energy Deployment

During FY 2015, INL invested $4.794M in 18 LDRD projects in support of the Enabling Clean Energy Deployment mission areas. The objective of this investment is to advance research in (a) clean energy generation and integration, (b) sustainable transportation, (c) efficient manufacturing, and (d) environmental stewardship.

Securing and Modernizing Critical Infrastructure

During FY 2015, INL invested $2.42M in 19 LDRD projects in support of DOE's Securing and Modernizing Critical Infrastructure mission areas:

- *Critical Infrastructure Protection.* The objective of this investment is to help advance INL's unique and differentiating capabilities in the technology focus areas of cybersecurity, industrial control system security, wireless communications spectrum sharing, power grid security, and material technologies. The investments focused on (a) critical infrastructure protection cybersecurity research that emphasized science-based innovative approaches for inter- and intra-system communication that assesses critical system and/or component vulnerabilities, and (b) building a secure, reliable, and resilient national grid, with reach focus on characterizing and prioritizing relevant cyber-physical threats to the power grid, developing a novel grid data analytics framework of metrics and operational data, researching new grid behaviors due to integration of variable generation/load, developing tools to assess cyber-physical vulnerabilities, and developing mitigations for critical infrastructure assets. In FY 2015, INL invested $1.3M in seven projects in this area.
- *Threat Analysis and Design Methodologies.* The objective of this investment is toward (a) concepts for characterizing and demonstrating previously unidentified threats or threat indicators for critical infrastructure, and (b) methodologies for translating threat information into metrics for prioritizing actions based on the significance of the type of threat, consequences if a threat is realized, or the reduction of threats by implementing protections. In FY 2015, INL invested $0.151M in two such projects.
- *All-Hazards Vulnerability Assessments and Cybersecurity for Industrial Controls:* The objective of this investment is to develop new INL capabilities that can be applied to future Department of Homeland Security critical infrastructure protection and resilience requirements. This includes security and resilience of industrial control systems; integration of cyber/physical/dependencies analyses; assurance of public safety communications; assessment of infrastructure vulnerabilities, dependencies/interdependencies, and resilience; and protection of infrastructure from all hazard threats. In FY 2015, INL invested $0.335M in two such projects.
- *Defense Systems.* The objective of this investment is to develop proof-of-principle concepts demonstrating blast and ballistic protection innovations to protect military personnel, critical infrastructure, and the public. This investment focused on developing concepts resulting in novel combinations of materials and design with the potential to enhance asset performance and protection against emerging threats. In FY 2015, INL invested $0.379M in four such projects.
- *Wireless National User Facility (WNUF)*. The objective of this investment is to advance the availability of the WNUF for commercial, federal/government, and academic broadband users. This LDRD investment seeks increased users at WNUF to explore the capacity and quality of services effects from cyber or physical vulnerabilities and to develop innovative mitigation solutions on wireless communication systems. The research focuses on (a) enhancing wireless security through experimental discovery and demonstration of how vulnerabilities and mitigation solutions can affect the capacity and quality of service of wireless systems that support critical infrastructure and emergency response, and (b) developing novel approaches for sharing spectrum among existing federal users and services while overcoming challenges in congestion management, managing spectrum sharing, developing new standards, and developing the testbed for broader applications. In FY 2015, INL invested $0.26M in one such project.

Report Organization

The remainder of this report is divided into three main sections, one for each of the three mission focus areas discussed above. These sections contain project write-ups that are arranged by project number, and each write-up contains (a) a description of the project, including its objectives and purpose; (b) a summary of the project's scientific or technical progress; and (3) a statement of the benefits that the project has provided to DOE national security missions and, if applicable, the missions of other federal agencies. Publications, presentations, invention disclosures, patents, and copyrights resulting from a project are also listed, as applicable.

ADVANCING NUCLEAR ENERGY

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15-023—Development of Stochastic 3D Soil Response Capability in MOOSE to Provide Design and Beyond-Design-Basis Seismic Motions for Nuclear Facilities

15-039—Transient Modeling of Integrated Nuclear Energy Systems with Thermal Energy Storage and Component Aging and Preliminary Model Validation via Experiment

15-040—Acoustic Telemetry Infrastructure for In-Pile ATR and TREAT Monitoring

15-060—Development of Efficient TREAT Modeling Capabilities with Graphite Data Improvement

15-071—Determination of Used Fuel Burnup through Fluorimetry of Activation Products

15-082—Advanced Fission-Chain and Multiplicity Analysis

15-094—Evaluation and Demonstration of the Integration of Safeguards, Safety, and Security by Design (3SBD)

15-141—Interfacing MOOSE Components to Enhance Capability

15-142—New In-Core Neutron Diagnostics at the University of New Mexico

15-143—Development of Bayesian Uncertainty Quantification Tools for Use in Complex Modeling and Simulation Code Validation

15-144—Investigation of Sonication-Assisted Electrolytic Reduction of Used Oxide Fuel in Molten Salt

15-145—Advanced Neutron and X-Ray Imaging at TREAT

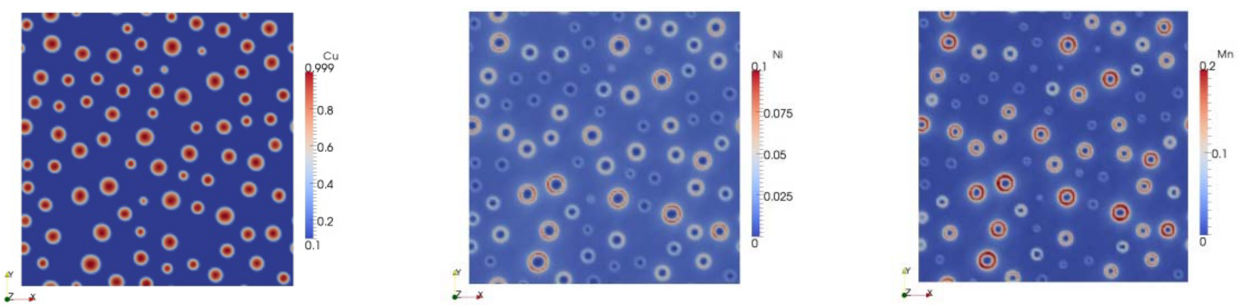
13-013—Development of a Micromechanistic Phase-Field Modeling Approach for the Life Estimation and Risk Assessment of Reactor Pressure Vessels

S. Bulent Biner, Yonfeng Zhang, and Pritam Chakraborty

The aim of this LDRD is to develop a micromechanically based phase-field modeling algorithm in which the evolution of microstructure due to radiation effects (i.e., precipitation of late blooming phases) and its effects on mechanical behavior can be simulated in a unified framework for aging reactor pressure vessel steels.

Summary

A phase-field algorithm based on the CALPHAD thermodynamic database was developed. Figure 1 shows the simulation result for an alloy containing 15at%Cu-1.5at%Ni and 1.5at%Mn annealed at 800 K. Experiments show that the initial precipitation starts as a metastable, body-centered-cubic phase, and the presence of other alloying elements, nickel and manganese, leads to the formation of a ring/core precipitate morphology, i.e., segregation of nickel and manganese around copper precipitates.



Cu Ni Mn

Figure 1. Precipitation morphologies obtained from phase-field model for Fe-15at%Cu-1.5at%Ni-1.5at%Mn for copper (left), for nickel (middle), and for manganese (right).

As can be seen from the figure, the simulation results closely follow the experimental observations.

The stability of precipitates and the role of the lattice defects in dilute iron-copper-nickel-manganese alloys for up to 1at%Cu concentrations were studied parametrically. The results show that the copper precipitates smaller than 2 nm are unstable and dissolve in the matrix. On the other hand, lattice defects—vacancy loops, self-interstitials, self-interstitial atoms, loops, and dislocations—can be heterogeneous nucleation sites leading to the formation of stable precipitates, as shown in Figure 2. In addition, it appears that the vacancy loops are stronger sinks than their counterpart, self-interstitial loops.

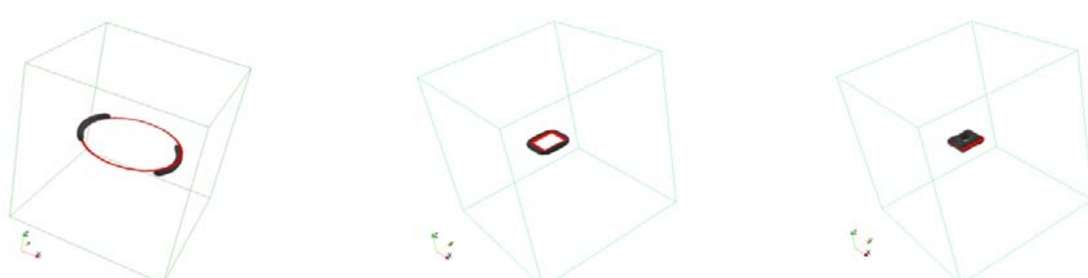


Figure 2. Precipitation behavior of Fe-1at%Cu-1at%Ni-1at%Mn at lattice defects. The black regions represent the copper precipitates for 100-nm-diameter dislocation loop (left); for 5-nm self-interstitial atom loop (middle); and 5-nm vacancy loop (right).

To simulate the hardening behavior resulting from the precipitates in reactor pressure vessel steels, a three-dimensional dislocation-dynamics algorithm within the formulation of the phase-field method was developed. In the algorithm, the large-scale evolution of dislocation densities can be easily accounted for, as shown in Figure 3.

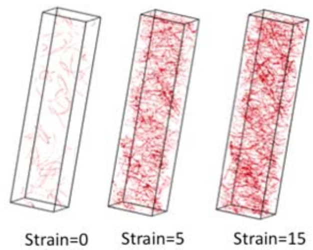


Figure 3. Evolution of dislocation density with 15% uniform axial strain in body-centered cubic iron from initial dislocation density (right).

The same algorithm was also used to simulate the interaction of gliding dislocations with copper precipitates in order to establish the hardening behavior, as shown in Figure 4. The kinetics of the interactions qualitatively agrees with the experimental observations; however, for quantitative results, the molecular dynamics simulations are required for the calibration of the parameters that appear in the phase-field model.

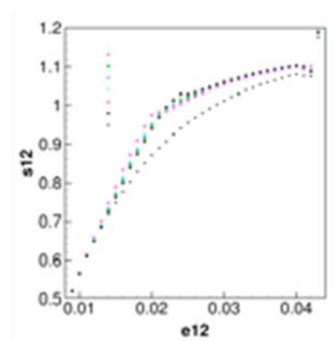


Figure 4. Phase-field simulation of interaction of an edge dislocation with a copper precipitate in iron (left) and resulting increase in the flow stress (hardening) (right).

Benefits to DOE

For life assessment of current light-water reactors to 60 years and beyond, it appears that the only viable option is predictive modeling along with the limited experiments. From the results presented above, it seems that a unified phase-field modeling approach (i.e., precipitation kinetics and the resulting hardening behavior), supplemented with the thermodynamic database and atomistic studies, may provide such a pathway.

Publications

Biner, S. B., Weifeng Rao, and Yonfeng Zhang, "The stability of precipitates and the role of lattice defects in Fe-1at%Cu-1at%Ni-1at%Mn alloy: A Phase-Field model study," *Journal of Nuclear Materials*, accepted.

Presentations

Biner, S. Bulent and Yongfeng Zhang, "A phase-field model study for precipitation behavior of a dilute Fe-Cu-Mn-Ni alloy," NUMAT-2014, Clearwater, Florida.

Rao, Wei-Feng, Yongfeng Zhang, and S. Bulent Biner, "The role of lattice defects on segregation/precipitation behavior of a dilute Fe-Cu-Mn-Ni alloys," SMINS-3 Workshop, October 2013, Idaho Falls, Idaho.

13-029—In-Pile Detection of Crack Growth in the ATR

A. Joe Palmer, Sebastien Teysseyre, Kurt Davis, Joy Rempe,[1] Gordon Kohse,[2] David Carpenter,[2] Yakov Ostrovsky,[2] and Steinar Solstad[3]

A key component in evaluating the ability of light-water reactors to operate beyond 60 years is characterizing the degradation of materials exposed to radiation and various water chemistries. Of particular concern is the response of reactor materials to irradiation-assisted stress corrosion cracking. Some test reactors outside the United States, such as the Halden Boiling Water Reactor, have developed a technique to measure crack growth propagation during irradiation (see Figure 1). This technique incorporates a compact loading mechanism to stress the specimen during irradiation. A crack in the specimen is monitored using a reversing direct-current potential drop (DCPD) method, which consists of introducing a precisely controlled current across a loaded specimen and measuring the drop in voltage across the crack mouth (which changes as a function of crack growth). This 3-year project applies the techniques used at the Halden Boiling Water Reactor to develop and evaluate a test rig design that can be used in U.S. material testing reactors, such as INL's ATR and the Massachusetts Institute of Technology Research Reactor (MITR). At this stage, the effort is focused on the engineering required to implement the technique, but not the testing of any specific materials.

Summary

The first year of this project (FY 2013) was devoted to designing, analyzing, fabricating, and benchtop testing a mechanism capable of applying a controlled stress to specimens while they are irradiated in a pressurized-water loop (simulating pressurized-water reactor conditions). Results from benchtop testing were encouraging and showed that the load applied to the specimen could be predicted accurately for various pressures supplied to the bellows.

During FY 2014, the second year of the project, the mechanism was used to fatigue a specimen in air that had been instrumented with DCPD connections. The process produced a linear crack rate, as shown in Figure 2. The specimen was then placed in a numerically controlled Instron machine. The control algorithm for the Instron machine was designed to match the calculated load applied by the loading mechanism (no direct measurement of load is possible with the loading mechanism). The crack rate obtained by the Instron machine was within 10% of that obtained using the loading mechanism, indicating that the loading mechanism was providing the predicted forces based on the magnitude of the fluctuating pressure applied to the bellows.

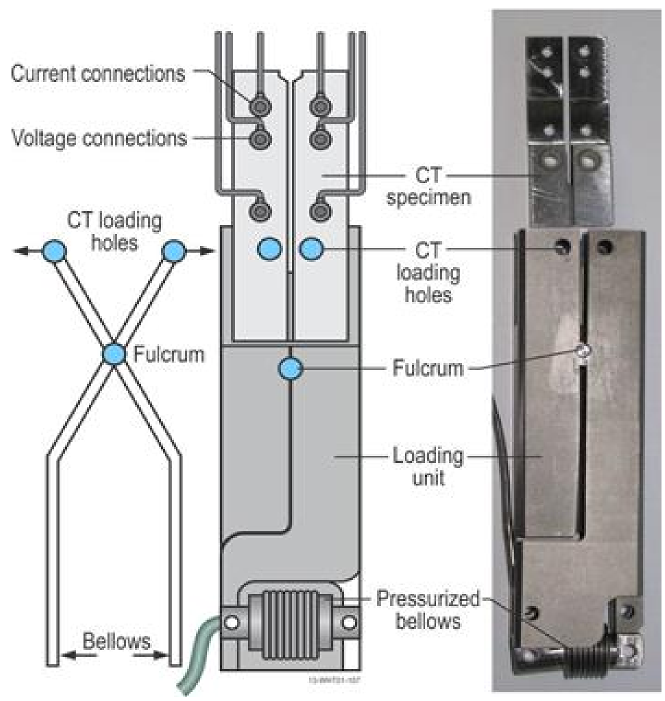


Figure 1. Schematic of a loading mechanism with direct-current potential drop connections.

[1] Rempe and Associates

[2] Massachusetts Institute of Technology Nuclear Reactor Laboratory

[3] Halden Reactor Project

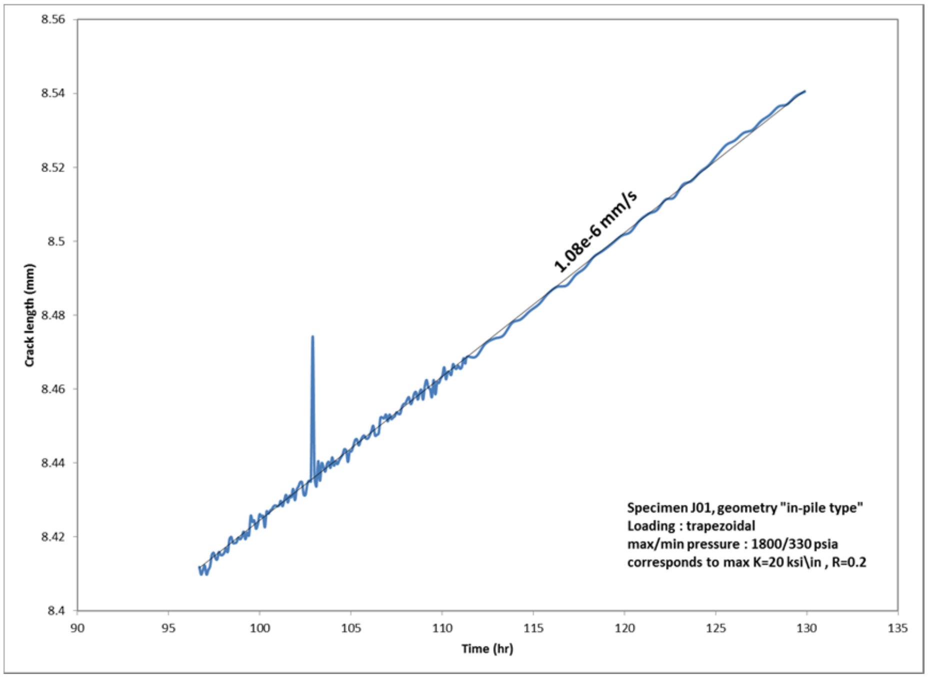


Figure 2. Crack length versus time obtained when fatiguing the specimen with the loading mechanism.

Also during FY 2014, most of the necessary documentation and safety reviews for testing in the MITR were completed.

FY 2015 was the final year of the project, and all aspects of the project came together for a successful conclusion. Early in FY 2015, the loading mechanism was extensively tested in one of the autoclaves at INL's High-Temperature Test Laboratory. Prior to installation in the autoclave, the specimen had been pre-cracked about 1.8 mm using an Instron machine, and then this crack was driven what appeared to be an additional 1.7 mm while in the autoclave (based on the voltage rise from the from the DCPD system). Subsequently, the specimen was opened, and the crack that was produced while in the autoclave was measured. The measured length was 1.695 mm, a nearly identical match to the DCPD-inferred crack length (see Figure 3).

After completion of out-of-pile autoclave testing, the test rig was installed in the MITR in May 2015 and irradiated until July 28, 2015. The results of this testing are shown in Figure 4. In this figure, the voltage rise on Channel 1 (Ch1) is indicated by the light blue data trace. Outside of the reactor environment, the crack growth is proportional to voltage change on this channel. This voltage change is essentially a measurement of the resistance change from one side of the specimen to the other as the crack propagates. However, in the in-pile environment, the electrical resistance of the specimen material itself increases due to dislocations and lattice vacancies from fast neutron damage. As seen in Figure 4, around Day 30 the specimen was not being cycled; however, the reactor was on, and a distinct upward trend in the Ch1 voltage is apparent, indicating a material property change and not an extension of the crack. This effect had been anticipated, and there were two voltage connections to the specimen, Ch1 and Channel 2 (Ch2). These two connections allowed removal of the portion of the voltage increase due to material property changes. The dark blue data in the Figure 4 labeled $Ch1_{crack}$ are these compensated data. The crack extension is proportional to $Ch1_{crack}$ and is represented by the dark orange data trace labeled "Crack Growth." The crack extension calculated for the entire test period in the reactor was 2.167 mm.

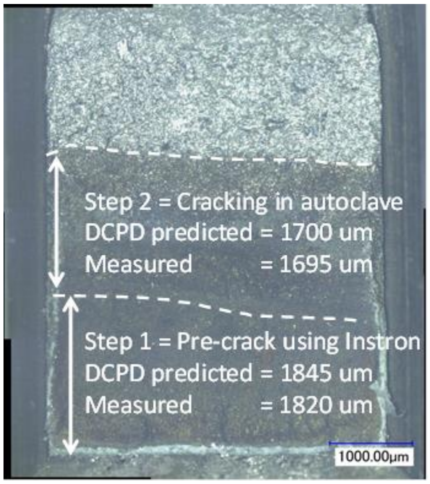


Figure 3. Measurement of crack produced in autoclave.

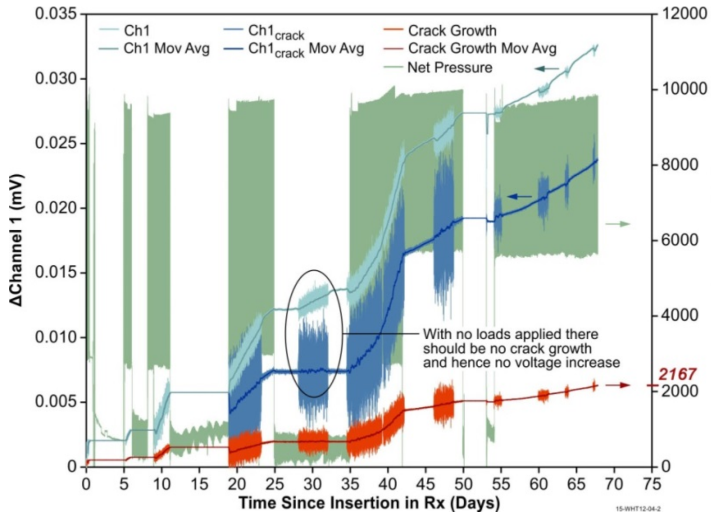


Figure 4. DCPD data gathered during irradiation in MITR.

After irradiation, the test rig was transferred to the Massachusetts Institute of Technology hot cell. A source of pneumatic pressure was used to actuate the loader again to pry open the crack, and the crack was photographed using a calibrated camera (see Figure 5). The total crack length was measured at 3.99 mm, as shown in Figure 6. The pre-crack length for this specimen was 1.8 mm, so the length of the crack driven while in the reactor was 3.99 mm – 1.8 mm = 2.19 mm, which is in excellent agreement with the 2.167 mm calculated from the DCPD signals.

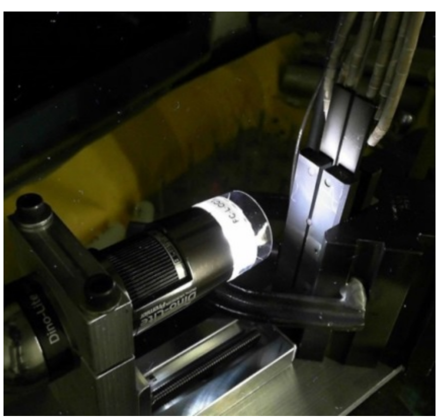


Figure 5. Hot cell photography setup.

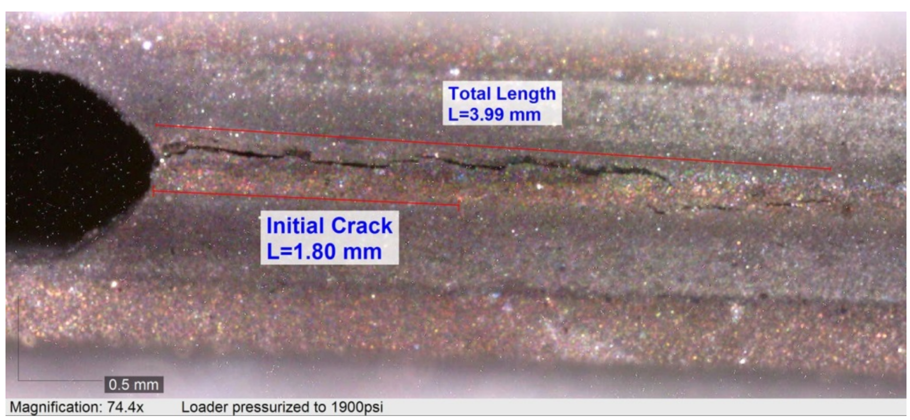


Figure 6. Micrograph of crack in specimen.

This successful conclusion demonstrated that the test rig, associated electronics, and software all performed as intended. This project has reduced the barriers for material scientists to utilize the technique, and the system is now available for use.

Benefit to DOE

Development of advanced in-core instrumentation is critical to DOE's energy security mission to provide world-class facilities for advancing nuclear science and technology. Successful completion of this effort will result in a proven crack-growth test rig that can be used by DOE-NE researchers and industry organizations to obtain real-time data for crack growth during irradiation testing in U.S. high-flux, material-testing reactors. This research also helped fund an INL employee completing a University of Idaho graduate degree.

Publications

Rempe, J., D. Knudson, J. Daw, T. Unruh, B. Chase, K. Davis, A. Palmer, and R. Schley, "Advanced In-pile Instrumentation for Materials Testing Reactors," *IEEE Transactions on Nuclear Science,* Vol. 61, pp. 1984-1994, August 2014.

Presentations

Kohse, G., A. Palmer, S. Teysseyre, D. Carpenter, Y. Ostrovsky, K. Davis, and J. Rempe, "Further Development of Crack Growth Detection Techniques for US Test and Research Reactors," 2015 Conference on Advancements in Nuclear Instrumentation, Measurements Methods (ANIMMA 2015), Lisbon, Portugal, April 20-24, 2015.

Palmer, A., S. Teysseyre, K. Davis, J. Rempe, G. Kohse, Y. Ostrovsky, and D. Carpenter, "Adaptation of Crack Growth Detection Techniques to US Material Test Reactors," International Congress on Advances in Nuclear Power Plants 2014 (ICAPP-14), Charlotte, North Carolina, April 6–9, 2014.

Rempe, J., D. Knudson, J. Daw, T. Unruh, B. Chase, K. Davis, A. Palmer, and R. Schley, "Advanced In-pile Instrumentation for Materials Testing Reactors," 2013 Conference on Advancements in Nuclear Instrumentation, Measurements Methods (ANIMMA 2013), Marseilles, France, June 23–27, 2013.

13-032—Experimental and Computational Analysis of Hydride Microstructures in Zirconium in Dry Storage Conditions

Mark Carroll, Laura Carroll, Richard Williamson, Jason Hales, Daniel Schwen, Jacob Bair, and Michael Tonks

During reactor operation, the radiolysis of coolant water and oxidation of the Zircaloy cladding at the cladding/coolant interface results in hydrogen production. Due to its low solubility in Zircaloy, this free hydrogen in the coolant is readily picked up by the cladding and results in the formation of brittle hydrides in the cladding bulk. While these hydrides do not significantly impact the in-service performance of modern reactors, there is considerable concern that hydrides may significantly impact the containment strength of the cladding during long-term storage of used fuel. The underlying reason hydrides are not an issue with regard to cladding integrity during reactor operation is that the hydrides primarily form in a relatively benign circumferential orientation in the cladding. Following operation and removal from the reactor, the used fuel rods are stored in pools and then go through a drying process. During the natural temperature excursions of this process, a fraction of the hydrides dissolve and reform in a preferential radial orientation due to stresses from the higher pressure inside the fuel rod. This radial orientation is considerably more problematic, because it provides an easy crack path along the hydrides that can lead to through-wall cladding failure. The purpose of this project is to develop a macroscale model that predicts the hydride orientation as a function of the stress and irradiation history. To accomplish this, a coupled experimental and simulation approach is taken in which a mesoscale model of hydride formation is developed while fundamental experiments are conducted on unirradiated samples of hydrided zirconium and Zircaloy. This macroscale model will be used in INL's BISON fuel performance code to predict the impact of hydride reorientation on cladding integrity under used fuel dry-storage conditions.

Summary

The project has been executed from the outset as two parallel efforts composing an advanced modeling component and a microstructure-based experimental component. A model has been developed that predicts the formation and growth of the common δ hydride phase in the zirconium alloy. To model the common δ-phase hydride in zirconium cladding, a phase field model has been successfully deployed that utilizes INL's mesoscale MARMOT code. The resulting model is specific to the evolution of the δ-hydride phase in α-Zr using thermodynamic free energies and experimentally measured lattice mismatches between the two constituents. The impact of applied stress on the hydride formation was investigated, and preliminary results of this model coupling in the elastic free energy due to lattice mismatch are shown in Figure 1.

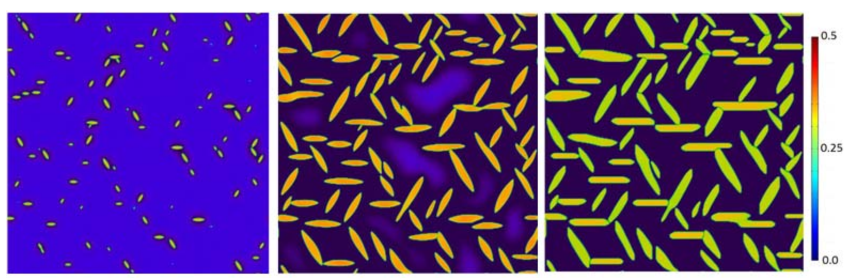


Figure 1. An example of a phase field quench simulation with temperature linearly decreasing from 630 K to 300 K.

The complex macroscopic structure of the δ-hydride phase in zirconium has also been experimentally isolated, characterized, and related mechanistically to nucleation and growth. Electron backscatter diffraction analysis of the extended δ-$ZrH_{1.66}$ structures in pure zirconium reveals that these structures consist of multiple interconnected precipitates of distinctly related orientations, as shown in Figure 2. These analyses confirm the expected $(0001)_{\alpha\text{-}Zr}//(111)_{\delta\text{-}ZrH1.66}$ orientation relationship between the hydride and the surrounding zirconium matrix grains. The δ-$ZrH_{1.66}$ precipitates do not extend in a discrete crystalline orientation but are regularly divided by 60-degree Type {111} twins in which adjacent δ-$ZrH_{1.66}$ grains share a {111} plane. Each hydride shares the latter orientation relationship (OR) with one of the adjacent α-Zr grains and a close-packed {111} plane with adjacent hydride precipitates. Developing an understanding of how the individual hydrides collectively form an interconnected hydride is critical to modeling hydride growth and reorientation.

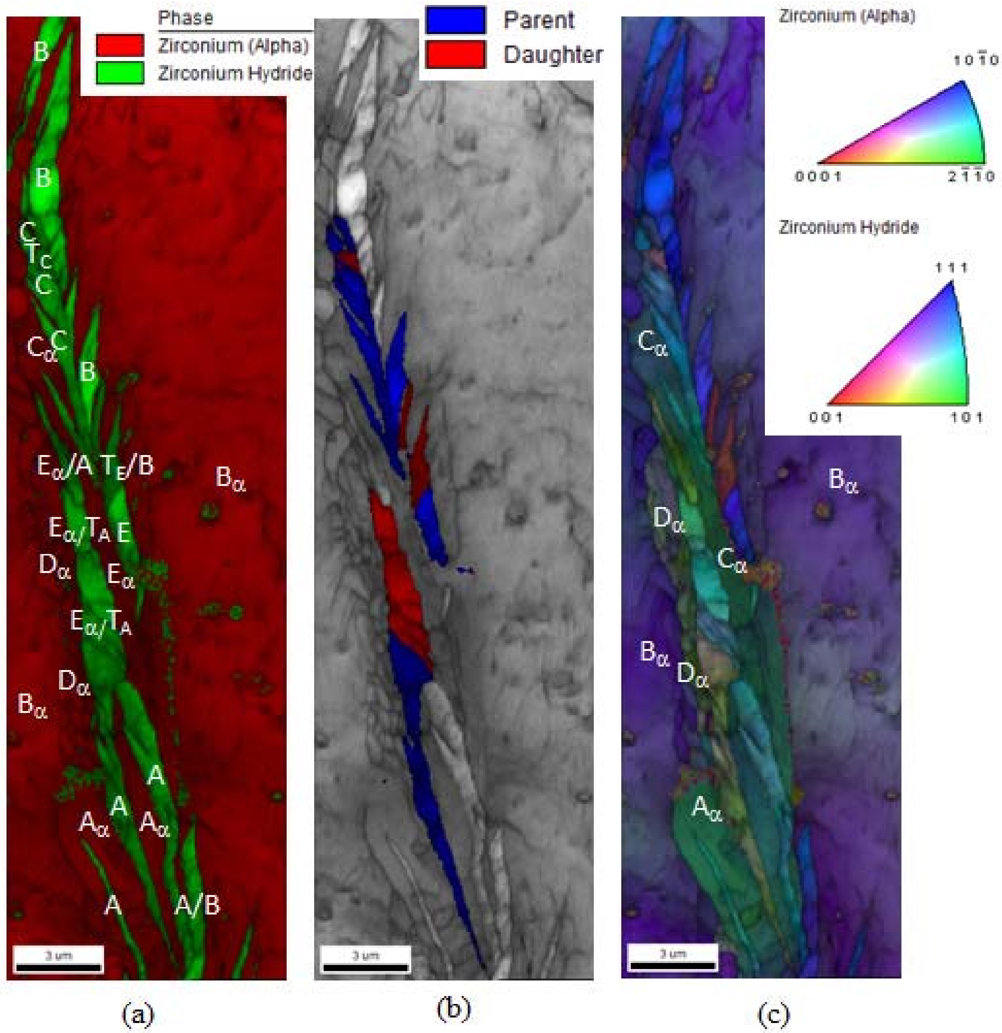


Figure 2. Example of the detailed characterization of an intra-granular δ-hydride in unalloyed zirconium with (a) the phase map, (b) 60-degree {111} twin parent/daughter superimposed on the IQ map, and (c) the inverse pole figure. The phase map in (a) is coded based on the OR of the α-Zr grains (labeled A_α, B_α, C_α, and D_α) and the corresponding hydride precipitate (A_δ, B_δ, C_δ, or D_δ) with which it exhibits the $(0001)_{\alpha\text{-Zr}}//(111)_{\delta\text{-ZrH1.66}}$ OR. Twinned hydrides are labeled with T_A such that the subscript denotes the hydride precipitate from which its orientation originates.

Benefit to DOE

This project provides the basis for a complex material model with the necessary complexity to enable the prediction of the impact of hydride formation and reorientation on zirconium-based nuclear cladding integrity under long-term dry storage conditions. The safe long-term storage of used fuel is of great interest to the DOE-NE Used Nuclear Fuel Disposition program, Electrical Power Research Institute, reactor vendors, and the major utilities.

Publications

Bair, J., M. Asle Zaeem, and M. Tonks, "A Phase-Field Model to Study the Effects of Temperature Change on Nucleation and Growth of γ-Hydrides in Zirconium," *Computational Materials Science*, in preparation.

Carroll, L. J., M. Tonks, T. M. Lillo, B. Fromm, D. C. Haggard, T. Morris, D. Swank, T. Trowbridge, and M. C. Carroll, "Characteristics of Interconnected δ-Hydride Precipitates in Zr," *Scripta Materialia*, in preparation.

Presentations

Carroll, M., L. Carroll, B. Fromm, W. Swank, D. Haggard, and M. Tonks, "Characterization of Delta Hydride Precipitates in Pure Zr and Zr-4," *TMS 2015 144th Annual Meeting and Exhibition*, Orlando, Florida, February 15–19, 2015.

13-033—Magnetic Separation Nanotechnology for Spent Nuclear Fuel Recycle

Leigh R. Martin, You Qiang,[1] Yaqiao Wu,[2] and Paul Benny[3]

The goal of this project was to develop an understanding of the usefulness of functionalized magnetic nanoparticles (MNPs) in used nuclear fuel separations, in particular minor actinide (An^{3+})/lanthanide (Ln^{3+}) separations and environmental remediation applications. The project aimed to characterize the physical and chemical properties of the ligand-functionalized MNPs (size, shape, aggregation, magnetization, etc.) using electron microscopy, transmission electron microscopy, a vibrating sample magnetometer, a localized electron atom probe, and simple solid liquid partitioning experiments with a variety of nuclides.

Summary

In FY 2015, the final year of the project, the research switched focus from used nuclear fuel and existing environmental wastes to application of the magnetic nanoparticle to the remediation of technetium. Tc-99 is a primary radionuclide (~6%) formed during the U-235 fission process. Typically found as an anionic pertechnetate species (TcO_4^-), it presents several challenges in the reprocessing waste stream due to its similarities to nitrate anion, interference in the plutonium-uranium extraction process, and poor behavior in glass vitrification. To address these issues, a surface-modified material (SMM) for the selective removal of TcO_4^- was developed for application with magnetic nanoparticles for facile separation of technetium from the aqueous waste stream (Figure 1). A solid-phase material was modified to specifically extract TcO_4^- based on previous studies in the Benny Laboratory at Washington State University.

Figure 1. Overview of the separation of technetium.

The general experimental approach involved using batch separation studies with the SMM to determine the overall performance to extract $^{99m}TcO_4^-$ from aqueous solutions. An initial equilibrium study examined the function of the SMM to remove $^{99m}TcO_4^-$ from solution (pH 4.0, 1.0 mM acetate) as a function of contact time (0-3 hours) (Figure 2). At relatively low concentrations of SMM (5 mg/mL), greater than 95.9 ± 1.8% of TcO_4^- was associated with SMM within 2 minutes, and quantitative removal occurred within 10 minutes (99.5 ± 0.2%). To determine the overall loading capacity/saturation point of the SMM, the concentration of TcO_4^- was increased from 3.8×10^{-13} to 0.1 M to determine the percent associated with the SMM and the remaining solution at a 10-minute equilibration time (Figure 3). To reach a relative high concentration of TcO_4^- while maintaining the concentration as low as reasonably achievable, macroscale stock MO_4^- solutions were prepared with nonradioactive perrhenate (ReO_4^-) and tracer levels of $^{99m}TcO_4^-$ (0.01, 0.1 µCi). The similar size and behavior of

[1] University of Idaho

[2] Boise State University/Center for Advanced Energy Studies

[3] Washington State University

rhenium and technetium oxoanions provide an analogous species for evaluation without a high radiation field, because no redox chemistry is involved. Quantitative sorption of MO_4^- was observed from tracer level 3.8×10^{-13} M to 1.0×10^{-4} M, providing a reasonably broad working range ideal for reprocessing applications in a waste stream (~100 ppm TcO_4^-).

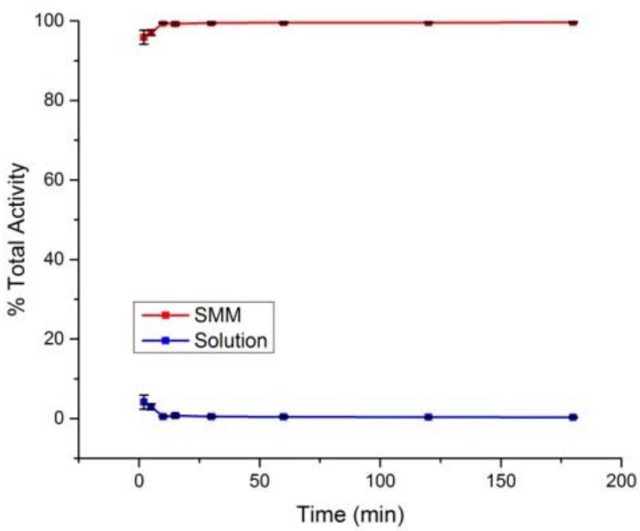


Figure 2. Adsorption equilibration time of TcO_4^- on the SMM.

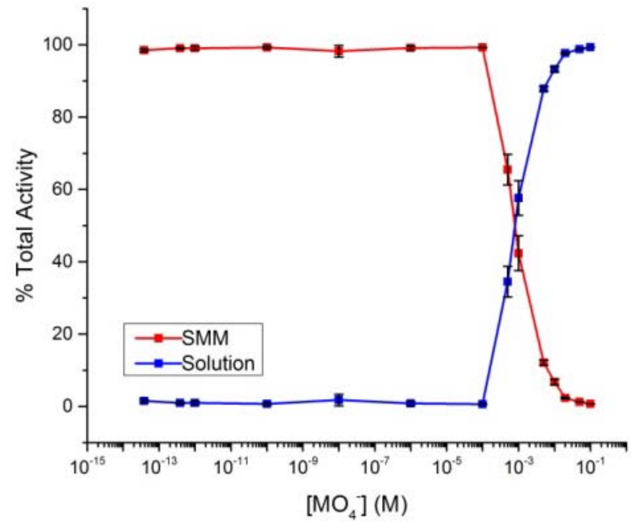


Figure 3. Saturation of SMM with different MO_4^- concentrations at 10-minute equilibration time.

The impact of $[H^+]$ or $[OH^-]$ on the TcO_4^- extraction behavior of the SMM was also evaluated to determine the efficacy of the material over a pH range. Experiments were conducted at $[MO_4^-] = 5.0\times10^{-4}$ M to generate a ~50% adsorption of MO_4^- to investigate potential synergistic interactions of pH with MO_4^- extraction. In the pH range (2–9) examined after a 10-minute equilibration, no statistically significant difference was observed between the acidic and alkaline conditions on the adsorption of MO_4^- to the SMM.

In the complex nature of spent nuclear fuel reprocessing streams, competing anions can potentially limit the overall effectiveness of TcO_4^- extraction with the SMM. Several common anions (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-, ClO_4^-) were examined as a function of anion concentration on the TcO_4^- extraction (Figure 4). Anions (Cl^-, SO_4^{2-}, PO_4^{3-}) exhibited limited competition with TcO_4^- at high concentrations ($[Cl^-]$ 1.0 M, $[SO_4^{2-}]$ 0.1 M, $[PO_4^{3-}]$ 0.5 M) with greater than 90% retention of TcO_4^- extraction on the SMM. Most similar in size and charge to TcO_4^-, concentration studies with NO_2^-, NO_3^-, and ClO_4^- yielded a more pronounced competition with TcO_4^- for available sites on the SMM. At 50% adsorption at 0.01 M, $[ClO_4^-]$ had the highest competition with TcO_4^-; however, this anion is not typically utilized in reprocessing scenarios. NO_3^- and NO_2^- also exhibited competition with TcO_4^- at higher concentrations at 50% adsorption of 1.3 and

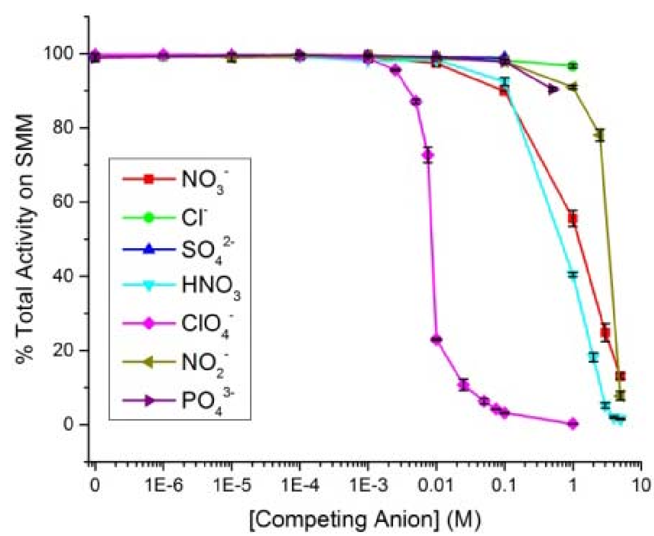


Figure 4. Competition studies with selected anions for TcO_4^- adsorption on SMM.

3.0 M, respectively. A competition study was also extended to different concentrations of HNO_3 (1.0×10^{-5} – 5.0 M) to mimic potential plutonium-uranium extraction raffinates. HNO_3 had a slight increase in competition over NO_3^-, with a 50% adsorption at 1.0 M.

Future studies involving the SMM will examine the impact of a reprocessing simulant solution and reprocessed tank waste to mimic conditions that would be encountered during the reprocessing streams, where multiple anions are competing simultaneously.

Benefits to DOE

The study of MNPs for minor actinide/lanthanide separations and technetium remediation activities has provided promising results in the application of these materials in separations relating to used fuel separations, technetium remediation, and critical material recovery from waste streams. This work has the potential to contribute to the design of an advanced fuel cycle, safe and effective cleanup of DOE contaminated sites, and cost-effective recovery of metal ions in solution from mining and ore-refining activities.

Publications

Bottorff, Shalina C., Thomas R. Hayes, Leigh R. Martin, and Paul D. Benny, "Efficiency Aqueous Extraction of Pertechnetate of a Novel Solid Phase," in preparation (waiting on provisional patent).

Bottorff, Shalina C., Thomas R. Hayes, Leigh R. Martin, and Paul D. Benny, "Efficient Extraction of Pertechnetate from Spent Nuclear Fuel," in preparation (waiting on provisional patent).

Bottorff, Shalina C., Huijin Zhang, Thomas R. Hayes, You Qiang, Leigh R. Martin, and Paul D. Benny, "High Efficiency Aqueous Extraction of Pertechnetate Using Magnetic Separations," in preparation (waiting on provisional patent).

Zhang, Huijin, Rocklan McDowell, Leigh Martin, and You Qiang, "Lanthanide Removal Characteristics from Aqueous Solution by DTPA-Functionalized Magnetic Nanosorbents," in review for *Environmental Science and Technology*.

Presentations

Benny, Paul D., You Qiang, and Leigh R. Martin, "High-efficiency aqueous extraction of pertechnetate of a novel solid phase," American Chemical Society, San Diego, California, March 2016, accepted.

Qiang, You, "Advanced Magnetic Separation Nanotechnology for Used Nuclear Fuel Recycling," Malcolm M. Renfrew Interdisciplinary Colloquium, University of Idaho, August 26, 2014.

Qiang, You, "Nanotechnology for Used Nuclear Fuel Recycle," *25th Annual Symposium of the PNWAVS Science and Technology Society*, Richland, Washington, September 16–19, 2014.

Qiang, Y. and H. Zhang, "Magnetic separation nanotechnology for recycling used nuclear fuel," Environment, Agriculture, Resources, Technology and Society (EARThS) Interdisciplinary Conference, Pullman, Washington, April 11, 2015.

Qiang, You, Huijin Zhang, Leigh Martin, and Terry Todd, "Magnetic Separation Nanotechnology for Nuclear Waste Recycle," Materials Science & Technology 2014, Pittsburgh, Pennsylvania, October 12–16, 2014.

Wu, Y., M. Kaur, and T. Todd, "Magnetic Cr-doped Fe-Fe oxide core-shell nanoparticles for used nuclear fuel separation," 2015 TMS 144th Annual Meeting and Exhibition, March 15–19, 2015, Orlando, Florida.

Zhang, H., L. Martin, Y. Wu, and Y. Qiang, "Magnetic nanosorbents for recycling spent nuclear fuel," 2015 TMS 144th Annual Meeting and Exhibition, Orlando, Florida, March 15–19, 2015.

Zhang, H. and Y. Qiang, "Magnetic separation nanotechnology for heavy metal treatment in industrial wastewater," Environment, Agriculture, Resources, Technology and Society (EARThS) Interdisciplinary Conference, Pullman, Washington, April 11, 2015.

Zhang, H., R. McDowell, L. Martin, and Y. Qiang, "Removal of actinides and lanthanides from aqueous solution by DTPA-functionalized magnetic nanosorbents," 16th Annual Meeting of the Northwest Section of the American Physical Society, Pullman, Washington, May 14–16, 2015.

Zhang, H., T. Xing, and Y. Qiang, "Magnetic nanosorbents for heavy metal and radioactive waste treatment," Materials Science & Technology 2014, Pittsburgh, Pennsylvania, October 12–16, 2014.

Patents

Benny, Paul D., You Qiang, and Leigh R. Martin, Technetium Extraction from Aqueous Solutions, provisional patent filed (Application No. 62237169).

13-035—Development of New Molten Salt Sensor Technology for Application to Safeguarding Pyroprocessing

Ken Bateman, Robert Hoover, Michael Shaltry, Michael Simpson,[1] Kerry Allahar,[2] Darryl Butt,[2] Supathorn Phongikaroon,[3] and Abraham Jurovitzki[1]

The need for DOE to safeguard its pyroprocessing facilities is increasing. Current state-of-the-art sensors are insufficient to provide real-time process monitoring of electrorefiners suitable to prevent diversion of fissile nuclear materials. This project involves the experimental investigation of various sensor technologies for application in monitoring the state of molten salt used for electrorefining in a pyroprocessing operation. Two different types of sensors have been investigated: (a) electrochemical and (b) spectroscopic. Application of these methods to molten salts is relatively new and involves significant challenges.

Summary

In the first year of the project, investigation was primarily focused on electrochemical monitoring using both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) via experiments with several different rare earth or actinide salts in molten LiCl-KCl. This included UCl_3, $ZrCl_4$, $LaCl_3$, and $CeCl_3$. Tests were run in the Radiochemistry Laboratory at the Center for Advanced Energy Studies as a collaborative effort between Boise State University and the University of Idaho. Signatures were recorded to distinguish between different species in the salt, and modeled time constants for EIS were found to depend on both the ion being measured and its concentration. These initial findings were presented at the 2013 TMS 142nd Annual Meeting and Exhibition.

In the second year of the project, a more in-depth electrochemical investigation was conducted of the LiCl-KCl-$SmCl_3$ system, which involves a soluble-soluble transition (Sm^{3+}/Sm^{2+}). Molten salt solutions consisting of eutectic LiCl-KCl and varying concentrations (0.5 to 3.0 wt%) of $SmCl_3$ were analyzed at 500^{o}C using both CV and EIS. For analyzing CV data, the Randles-Sevcik equation was employed. This equation relates CV peak height to concentration but also requires knowledge of the diffusion coefficient. Diffusion coefficients were thus measured by using this equation, CV data, and known concentrations. The results indicated significant variability in the diffusion coefficient over the range of concentrations, thus suggesting that CV has limited potential for a highly accurate determination of concentrations in the salt. This motivates the investigation of the EIS method. EIS spectra at the anodic, cathodic, and half-peak potentials were then measured. A six-element Voigt model was used to analyze the EIS data in terms of resistance-time constant pairs. The lowest resistances were observed at the half-peak potential with the associated resistance-time constant pairs characterizing the reversible reaction between Sm^{3+} and Sm^{2+}. Regressed model parameters were used to extrapolate to the polarization resistance. A polarization resistance-concentration relationship was determined that yielded bulk concentration values similar to experimental values. The clear advantage of this approach is that knowledge of the diffusion coefficients is not necessary to predict concentration based on electrochemical response.

In the final year of the project, the study was expanded to include ultraviolet/visible (UV/Vis) spectroscopy of molten salts. In this case, the objective was to demonstrate a near real-time method for analyzing the molten salt used for electrolytic reduction of oxide spent fuel. This process utilizes molten LiCl as the electrolyte salt rather than the LiCl-KCl used for electrorefining. Under normal operations, only a handful of fission products partition into the salt phase during processing of spent fuel. And those specific fission products (cesium, strontium, barium) are expected to be transparent to UV/Vis light. Misuse of the electrolytic reduction process could involve chlorinating actinides from the oxide to the chloride state, and process monitoring technology is needed to detect

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such misuse. An in situ chlorination of U_3O_8 and Nd_2O_3 from simulated spent fuel using $ZrCl_4$ was performed. Subsequently, analysis of the salt using inductively coupled plasma-optical emission spectrometry verified that soluble uranium and neodymium compounds had been formed that partitioned into the salt. CV and UV/Vis absorption was then tested to determine which method was most effective at detecting the presence of uranium and neodymium in the salt. To make the UV/Vis measurements, a high-temperature cell was designed and built to allow for molten salt to be analyzed. CV measurements clearly indicated the presence of U^{3+} and Nd^{3+} in the salt, while the UV/Vis measurements were hampered by high baseline absorption of the UV/Vis radiation. Further optimization of the UV/Vis measurement is needed to make it an effective method. Further analysis of CV data obtained using LiCl-KCl salts in the first two years of the project verified a concentration dependence of the diffusion coefficients for both $SmCl_3$ and $LaCl_3$ in LiCl-KCl. The analysis also indicated there is an Arrhenius-type temperature dependence to the diffusivity. In more complex salts, it was found that presence of different ions also affects diffusivity of a given ion of interest. These results support the conclusion that the use of CV data with diffusion-limited rate equations is subject to significant error for concentration measurements. This motivates the continued study of EIS, which generates information-rich data that are just beginning to be deciphered. The conclusion for moving forward is that electrochemical methods are most easily implemented in these molten salt processes. Direct measurement of actinide concentrations using CV is challenging due to variability of diffusion coefficients. EIS data may ultimately be more useful for concentration measurement, but more experimentation and data analysis are needed. In systems such as electrolytic reduction where any measurable concentration of actinides in the salt is a concern, the CV method is extremely useful for detecting process misuse.

Benefits to DOE

DOE's national security mission is to enhance nuclear security through defense, nonproliferation, and environmental efforts. This project directly contributed to the nonproliferation aspect of the DOE mission. This research enhanced technology capability to prevent proliferation of nuclear material from pyroprocessing-based fuel reprocessing systems. This project evaluated the applicability of electrochemical and spectroscopic methods to monitoring these systems. Results indicated that electrochemical methods are more readily implemented and deliver information-rich feedback that can be utilized in a variety of safeguards approaches for pyroprocessing.

Publications

Allahar, K., M. Shaltry, D. Butt, M. Simpson, S. Phongikaroon, and K. Bateman, "Electrical Impedance Spectroscopy and Cyclic Voltammetry Methods for Monitoring $SmCl_3$ Concentration in Molten LiCl-KCl Eutectic," in preparation for *Electroanalytical Chemistry*.

Jurovitzki, A., Wilson, E. Allred, C., Jeong, S. M., Bateman, K. J., and Simpson, M. F., "Chlorination of U_3O_8 and Nd_2O_3 using $ZrCl_4$ in molten LiCl," in preparation.

Presentations

Allahar, K., et al., "Electrochemical Impedance Spectroscopy Monitoring of $SmCl_3$ in LiCl-KCl Molten Salt," DOE MPACT Working Group Meeting, San Diego, California, March 18–20, 2014.

Jurovitzki, A., et al., "Chlorination of actinide and rare earth oxides for application to continuous pyrochemical reprocessing," Annual Meeting of the American Nuclear Society, San Antonio, Texas, June 2015.

Jurovitzki, A., et al., "Monitoring Fission Products and Actinide Levels during Pyroprocessing via UV-vis Absorption Spectroscopy," International Pyroprocessing Research Conference, Idaho Falls, Idaho, October 19–23, 2014.

Jurovitzki, A., et al., "Monitoring Pyroprocessing through Electrochemical Methods," Annual Meeting of the American Institute of Chemical Engineers, Atlanta, Georgia, November 17, 2014.

Simpson, M., et al., “Spectroscopic Real Time Monitoring of Molten Salts in Nuclear Electrorefiner Systems,” TMS 2014, San Diego, California, February 20, 2014.

Shaltry, M., et al., “Characterization of Samarium Chloride-Europium Chloride in Molten LiCl-KCl Eutectic by Electrical Impedance Spectroscopy,” TMS 2015 144th Annual Meeting and Exhibition, Orlando, Florida, February 15–19, 2015.

13-039—Induction-Based Fluidics Mass Spectrometry for Characterizing Radioactive Extraction Solvents

Gary S. Groenewold, Chris A. Zarzana, and Kristyn Johnson

Over the past several years, electrospray ionization (ESI)-mass spectrometry (MS) has been invaluable for characterizing the effects of radiation on solvent extraction systems used in fuel cycle separations. ESI functions by spraying droplets at a sampling aperture, transferring charged solutes into the gas phase where they can be analyzed by the MS. In conventional ESI-MS, the majority of the sample solution is deposited on the outside of the aperture. Usually this is inconsequential, but if the sample contains significant levels of radioactive contamination, radiological control requirements preclude the use of ESI-MS. The research objectives of this project are to minimize the volume of sample used and to improve the transfer efficiency into the mass spectrometer, thus achieving compatibility with radiological control requirements without compromising analytical quality.

Summary

Instrument development focused on interfacing a non-conductive nanoliter capillary with an ESI-MS. New technology referred to as induction-based fluidics was used to launch nanoliter-sized droplets directly into the ESI aperture, and experiments demonstrated that this could be accomplished without sample losses on the sides of the sampling aperture cone (Figure 1).

Figure 1. Close-up view of the capillary used to generate charged droplets, aligned with the sampling aperture cone of an ESI-MS instrument.

Experiments generated mass spectra of N,N-(diisobutylcarbamoyl)methyl,octyl,phenyl phosphine oxide (CMPO) derivatives (used in nuclear fuel cycle separations, Figure 2) and associated lanthanide coordination complexes. Sample volumes as small as 20 nL produced high-quality mass spectra, and not only that, the experiments could be pulsed at a rapid repetition rate, enabling very fast analyses if required to reduce dose. Experiments were then conducted that evaluated the efficacy of very low flow electrospray ionization, and similar high-quality data were generated by operating the flow as low as 4 µL per hour. Sample solutions having concentrations of 100 µmol/L produced excellent mass spectra at this flow rate, in 30 seconds or less; this corresponds to an absolute quantity of 0.3 pmol, a significant improvement over the single droplet approach. The remarkable sensitivity achieved indicated that the nanoliter-flow ESI-MS could very likely function within radiological control requirements at the INL's Central Facilities Area, so subsequent research focused on modifying an instrument for a radiological environment.

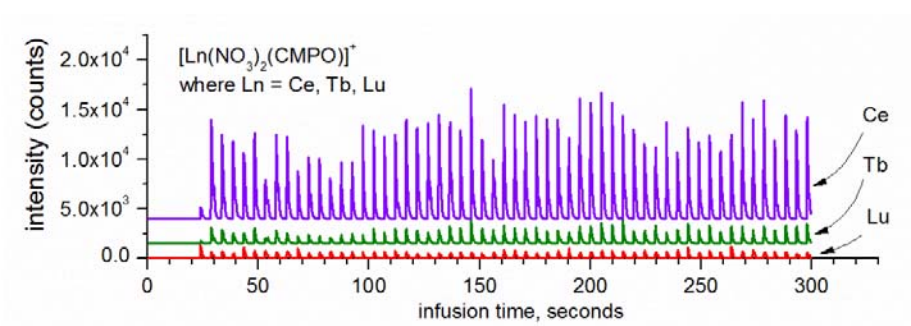

Figure 2. Temporal ion profiles generated from 50-nL droplets of a solution containing cerium, terbium, and lutetium with the nuclear fuel cycle extractant CMPO. Each peak represents a single nanodroplet, containing about 100 pmol of the metals.

Another objective is to replicate the chromatographic separation using a low-sample-volume, low-flow approach. Liquid chromatograph operations would be complicated in a radiological environment, so an electrospray capillary needle packed with a chromatographic stationary phase was developed to minimize volume and provide separation without any modification to the ESI experiment. A combined capillary column-ESI needle was specified and procured for separations experiments. Injection of 39×10^{-12} g (39 pg) of CMPO showed a defined chromate-graphic peak (Figure 3) sufficient for simple separations.

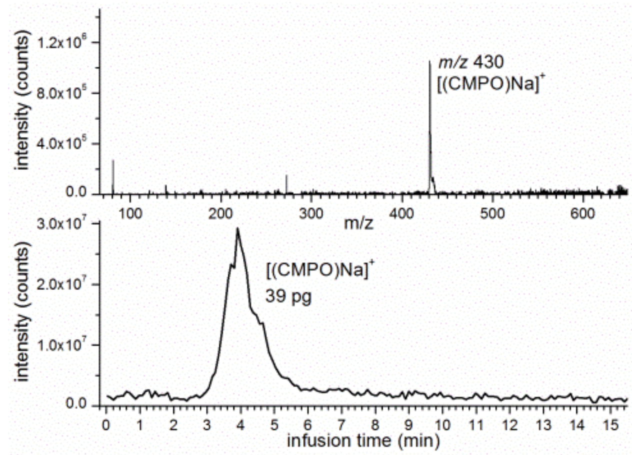

Figure 3. Top, mass spectrum, 39 pg of CMPO. Bottom, temporal ion profile of m/z 430.

A benchtop mass spectrometer was prepared for operation within radiological buffer areas at INL; the instrument was subjected to extensive maintenance and thoroughly benchmarked using nonradioactive samples. A laboratory instruction covering ESI-MS work control was written, reviewed, and approved, which enabled the instrument to be relocated to the Central Facilities Area, Building 625, Laboratory 240, within the radiological buffer area at that facility and proximate to a hood that is controlled as a radioactive contamination area.

Benefits to DOE

There is an ongoing need for the capability to chemically measure vanishingly small sample volumes of radioactive solutions in research conducted in each of the three INL mission areas: nuclear energy, national security, and sustainable energy. ESI-MS provides excellent information on the solution solutes but has not historically been compatible with radioactive samples, because the majority of the sample is deposited on the ESI source, where radioactive solutions constitute loose contamination. The induction-based fluidics project produced an ESI-MS instrument that will provide detailed molecular information for fuel-cycle separations without contaminating the exterior surfaces. The instrumentation will constitute a capability that is rare in the analytical-chemistry and radiochemistry communities and will significantly enhance INL's competitive position in the fuel cycle separations area and in process control, because the proposed technology is capable of solution analysis using exceedingly small volumes.

Publications

Groenewold, G., A. Sauter, Jr., and A. Sauter III, "Rapid Analysis of Single Droplets of Lanthanide-Ligand Solutions by Electrospray Ionization Mass Spectrometry Using an Induction Based Fluidics Source," *Analytical Chemistry*, Vol. 85, pp. 6398–6404, 2013.

13-050—Concurrent Atomistic to Macroscale Modeling of Materials under Irradiation Using the Phase Field Crystal Method

Yongfeng Zhang, S. Bulent Biner, Richard Williamson, Derek Gaston, Michael Tonks, Katsuyo Thornton,[1] and Dmitry Karpeev[2]

Because the fuel performance is usually evaluated at the engineering scale, many relevant material behaviors are governed by physics at the atomic scale or even the electron-scale resolution. To be quantitatively predictive, fuel performance codes need to be informed with relevant physics from various scales, rather than using empirical models. To date, tremendous effort has gone into developing multiscale modeling tools for predictive fuel performance simulations, including the MOOSE-BISON-MARMOT (MBM) approach at INL. The MBM takes atomic data as input via a hierarchical coupling and itself does not directly have an atomic scale capability. The objective of this project is to add direct atomic resolution to the MBM approach. As a result, several phase field crystal (PFC) models in the literature are implemented into the MOOSE framework. Fundamental developments in the PFC method have been created to correctly apply deformation for the calculation of elastic moduli and to represent the configuration and diffusion of vacancies for radiation damage. The progress made expands the modeling capabilities at INL within the MOOSE framework and improves the existing PFC models for mechanical properties and radiation damage. This LDRD has included work by two postdocs and a Ph.D. student at the University of Michigan and multiple interns at INL.

Summary

This LDRD started in FY 2013 and expired in FY 2015 (September 2015). During the three years of research, three PFC models have been successfully implemented into MARMOT and solved using the MOOSE framework. The implemented models include two polynomial models described in an article by Jaatinen and Ala-Nissila[3] and a rational functional fit model in Pisutha-Arnond et al. (2013).[4] In Figure 1, the solidification process of a three-dimensional, body-centered cubic iron lattice has been simulated using MOOSE with the eighth-order model described by Jaatinen and Ala-Nissila.[3] By linearly fitting the free-energy curves with respect to the atomic density, the elastic moduli can be obtained by applying various types of elastic deformation. Note that this effort represented the first one to solve PFC models using the finite-element method.

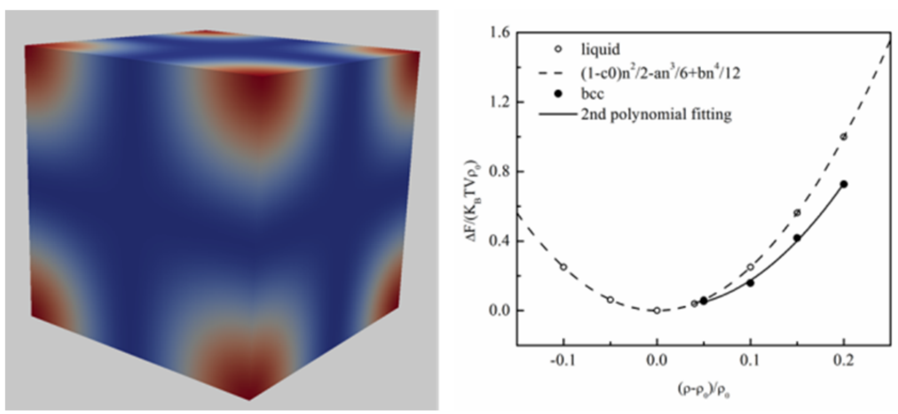

Figure 1. Stabilized bcc Fe lattice in a MARMOT simulation using the 8th order polynomial PFC model (left), and the free energy as a function of relative density. The bulk modulus can be obtained by parabolic fitting of the free energy curve (right).

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[1] Materials Science and Engineering Department, University of Michigan

[2] Mathematics and Computer Science, Argonne National Laboratory

[3] A. Jaatinen and T. Ala-Nissila, "Eighth-order phase-field-crystal model for two-dimensional crystallization," *Physical Review*, November 23, 2010.

[4] N. Pisutha-Arnond, V. Chan, M. Iyer, V. Gavini, and K. Thornton, "Classical density functional theory and the phase-field crystal method using a rational function to describe the two-body direct correlation function," *Physical Review E*, Vol. 87, 013313, January 30, 2013.

To solve the RFF model in MOOSE, a multigrid preconditioner has been developed to efficiently solve the Helmholtz problems using the finite-element method. The PFC models were initially implemented in MARMOT and have been moved to MOOSE the phase field module in FY 2015 to be accessed by external researchers in response to inquiries from multiple research groups on using MOOSE for PFC simulations.

Two approaches to applying mechanical deformation in PFC were developed to improve the commonly used approach in the literature, which evaluates the PFC free energies on coordinates mapped to desired deformed states. This straightforward method requires interpolation of the order parameters, which skews the computational domain for shear-type deformation. Two alternative approaches were explored to apply deformation robustly. The first approach maps the Laplacian operator in the PFC free energy from deformed to undeformed coordinates and does not require interpolation. The second method implements deformation via a scaling of the wave vectors. It is formulated in Fourier space and can be used when the PFC free energy is expressed in Fourier space. Both methods were found to be applicable for shear deformation. They are also shown to be accurate in predicting the elastic moduli of a body-centered cubic crystal and are useful to calibrate PFC models for mechanical properties.

In FY 2015, a new approach was developed to represent the configuration and diffusion of vacancies. Vacancy is one of the base units to measure radiation damage in materials. It is found that vacancies can be stabilized by adding a penalty term to the free energy for a negative-order parameter. Furthermore, by using a noise term mimicking atomic vibration, diffusion of individual vacancies via atomic jump (Figure 2) can be realized in PFC simulations. These results are crucial for simulating thermodynamic and kinetic behaviors of vacancies using the PFC method.

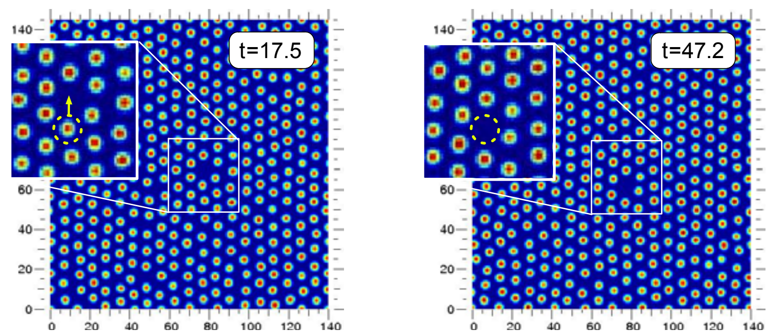

Figure 2. Snapshots from a PFC simulation showing the diffusion of a vacancy via atomic jump.

In addition, a novel technique to obtain an analytical direct-correlation function was developed to be used in the classical density functional theory. Some of the progress in model development was made in FY 2015 and will be implemented in MOOSE in the future.

Benefits to DOE

This project expands the MBM multiscale fuel performance toolkit by bringing in atomic-scale modeling capability. Such a capability provides an opportunity for concurrent modeling of radiation damage at the atomic level and the consequent change in material properties at the engineering level in the MBM approach. The research outcome will improve the predictive modeling of radiation damage and will help the design of advanced fuels and nuclear materials.

Publications

Chan, V., N. Pisutha-Arnond, and K. Thornton, “Numerical Implementation of Deformation in the Phase-Field Crystal Model,” under review.

Ghosh, S. and K. Thornton, “A Novel Technique to Obtain Analytical Direct Correlation Function for Use in Classical Density Functional Theory,” in preparation.

Montiel, D. and K. Thornton, “Diffusion of Individual Vacancies via Atomic Jump in the Vacancy Phase-Field Crystal Model,” in preparation.

Montiel, D. and K. Thornton, “Stability of Individual Vacancies in the Vacancy Phase-Field Crystal Model,” in preparation.

Presentations

Butterfield, A., V. Chan, Y. Zhang, M. Tonks, K. Thorton, and D. Karpeev, “Obtaining Elastic Constants Using Phase Field Crystal Modeling,” ANS Annual Meeting, Reno, Nevada, June 15–19, 2014.

Chan, V., N. Pisutha-Arnond, K. Elder, and K. Thornton, “Phase-Field Crystal Model and Thermodynamics of Elastically Stressed Solids,” Materials Science & Technology 2013 Meeting, Montreal, Canada, October 29, 2013.

Chan, V., N. Pisutha-Arnond, and K. Thornton, “Calculations of Isothermal Elastic Constants in a Classical DFT-Based Phase-Field Crystal Model,” U.S. National Congress on Theoretical and Applied Mechanics 2014, Lansing, Michigan, June 15–20, 2014 (invited).

Ghosh, S., V. Chan, and K. Thornton, “A Novel Approach to Obtain Approximate Analytical Direct Correlation Function for Use in Classical Density Functional Theory,” U.S. National Congress on Theoretical and Applied Mechanics 2014, Lansing, Michigan, June 15–20, 2014.

Montiel, D. and K. Thornton, “Energetics and Kinetics of the Vacancy Phase-Field Crystal Model,” 13th U.S. National Congress on Computational Mechanics, San Diego, California, July 2015.

Montiel, D. and K. Thornton, “Analysis of the Stability and Diffusion of Individual Vacancies Using the Vacancy Phase-Field Crystal Model,” TMS 2015 144th Annual Meeting and Exhibition, Orlando, Florida, March 2015.

13-060—Metal Fluoride Preparation for AMS Analysis

James E. Delmore, Gary S. Groenewold, and Chris A. Zarzana

INL researchers are developing new chemical approaches that will support measurements of isotope ratios that are used by U.S. and international organizations to ensure that nuclear energy facilities are operating in compliance with nonproliferation treaty commitments. The project's objective is to develop new means for converting elemental isotopes in environmental samples into negatively charged, fluorine-containing molecules called "fluoroanions" that are compatible with existing and emerging isotope ratio mass spectrometry instrumentation. If successful, the project will provide the scientific chemical basis for improved ultratrace isotope ratio measurement having better accuracy, lower detection limits, and reduced costs.

Summary

Experimental results from this research have demonstrated that unique fluoroanions of uranium, zirconium, iron, and silicon can be produced in high abundance with very low chemical background. These fluoroanions were produced by reacting oxides and salts of the metals with an ionic liquid, 1-ethyl-3-methylimidazolium fluorohydrogenate (EMF). After dilution with acetonitrile to make fluoroanion solutions, these compounds were analyzed using either electrospray ionization mass spectrometry or desorption chemical ionization mass spectrometry. The EMF sample was provided by INL collaboration with Tetsuya Tsuda (Osaka University) and Rika Hagiwara (Kyoto University).

Fluoroanions of both zirconium and iron were produced by mixing salts with the EMF ionic liquid and then diluting the resulting solution for electrospray ionization mass spectrometry analyses. The zirconyl cation ZrO^{2+} reacted to form ZrF_5^- in an efficient manner, indicating that the fluorohydrogenate anion would attack strongly bound metal-oxo species that will complicate isotope ratio measurements of actinides. Both Fe^{3+} and Fe^{2+} salts resulted in production of FeF_4^-, indicating that Fe(II) is oxidized. This theme was also observed when UO_2 and U_3O_8 were dissolved in EMF; in both instances, the resulting solution generated an exceptionally clean mass spectrum consisting principally of UF_6^- at *m/z* 352, which indicated oxidation of uranium from the +4 to the +5 state. The very low background seen in the mass spectra indicated sufficient dynamic range to enable measurement of the low abundance uranium isotopes.

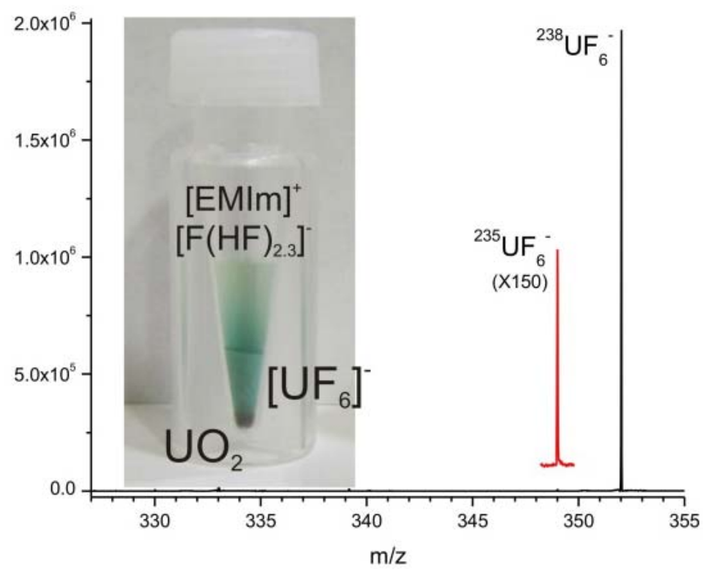

Figure 1. Photograph of an EMF-UO_2 solution; the green color indicates U(V). The mass spectrum of the solution shows the intense $^{238}UF_6^-$ and a much lower U-235 isotopic ion (left).

More recent studies addressed the ability of the EMF ionic liquid to dissolve mineral particulates that are likely to be representative sample types. Treatment of a mineral glass particle resulted in dissolution, producing principally SiF_5^-, with a lower intensity AlF_4^- and much less abundant fluoroanions of iron and calcium. The results showed that the ionic liquid was highly compatible with mineral dissolution, and that it could be performed using microliter volumes on particulate samples.

Benefits to DOE

The project developed a new approach for generating metal fluoroanions that may be highly compatible with making ultratrace isotope ratio measurements. Transitioning the fluoroanion formation chemistry into an accurate analytical isotope-ratio measurement method will enable the United States to make more informed nonproliferation policy decisions regarding the nonproliferation status of international nuclear energy programs at a substantially reduced cost compared with current methods. Improved measurement of isotope ratios at the ultratrace level will advance the DOE nonproliferation mission and elevate the global recognition of DOE's leadership position in nuclear and radiological science and measurement technologies.

Publications

Groenewold, Gary S., James E. Delmore, Michael T. Benson, Tetsuya Tsuda, and Rika Hagiwara, "Fluorohydrogenate Cluster Ions in the Gas Phase: Electrospray Ionization Mass Spectrometry of the [1-ethyl-3-methylimidazolium$^+$][$F(HF)_{2.3}^-$] Ionic Liquid," *Journal of Physical Chemistry A*, Vol. 117, pp. 14191-14199, 2013.

Groenewold, Gary S., James E. Delmore, Michael T. Benson, Tetsuya Tsuda, and Rika Hagiwara, "Generation of gas phase zirconium fluoroanions by electrospray of an ionic liquid," *Rapid Communications in Mass Spectrometry*, Vol. 26, pp. 1233–1242, 2014.

Zarzana, Chris A., Gary S. Groenewold, Michael T. Benson, James Delmore, Tetsuya Tsuda, and Rika Hagiwara, "Iron Fluoroanions and Their Clusters by Electrospray Ionization of a Fluorinating Ionic Liquid," *Journal of the American Society for Mass Spectrometry*, Vol. 26, pp. 1559–1569, 2015.

13-071—Advanced Fracture Modeling for Nuclear Fuel

Benjamin Spencer, Hai Huang, Jason Hales, Derek Gaston, and John Dolbow[1]

Fracture in ceramic nuclear fuel plays an important role in its thermal and mechanical behavior. Currently employed techniques for fracture modeling in fuel have well-known mesh dependencies. Improved fracture modeling for nuclear fuel is essential for predictive modeling of fuel behavior in conditions such as accidents, which are outside the range of applicability of current fuel behavior models. This project applies three fracture modeling techniques: the extended finite element method (XFEM), the discrete element method (DEM), and peridynamics to fuel performance modeling. These techniques are well known to overcome weaknesses of methods used in current practice but have had limited applications to multiphysics problems and have no, or very limited, application to nuclear fuel modeling. This project is making these methods available in the BISON nuclear fuel performance modeling code and is demonstrating their applicability to nuclear fuel simulation. This will strengthen the ability to predict fuel behavior in normal and accident conditions.

Summary

This three-year project, which was just completed, consisted of concurrent efforts to apply the XFEM, DEM, and peridynamics methods to model fracture in nuclear fuel. In XFEM, the standard finite element method is enhanced to permit it to model discontinuities in solution fields such as those that occur across a crack. The standard continuous finite element basis functions are enriched with discontinuous functions that enable cracks or other material interfaces to be dynamically inserted at arbitrary locations in the mesh; these interfaces do not have to coincide with element boundaries.

XFEM has been implemented in the MOOSE framework, upon which BISON is based, using the phantom node technique, a variant of XFEM in which elements containing discontinuities are split into two specially treated elements. A mesh-cutting algorithm was developed following the work of Richardson et al.[2] and incorporated into MOOSE. This algorithm currently supports crack growth and branching in two dimensions and stationary cracks in three dimensions. This has enabled a unique capability to solve arbitrary multiphysics problems with discontinuities represented with XFEM. This has been applied to two-dimensional BISON simulations of propagating cracks in nuclear fuel, as shown in Figure 1(a). The three-dimensional capability to model stationary cracks has been demonstrated with prescribed radial cracks in nuclear fuel, as shown in Figure 1(b). A capability to model crack initiation and growth in MOOSE using a combination of the phase field method and XFEM is demonstrated in Figure 1(c). This technique resolves some of the challenges in defining complex crack paths with XFEM.

This project also pursued DEM and peridynamics for modeling fracture in nuclear fuel. These methods both employ bonds between nodes to naturally represent arbitrary fracture as they are broken when a failure criterion has been met. In this project, a series of proof-of-concept, two-dimensional DEM simulations of fracture in nuclear fuel were performed using an existing research code. These simulations demonstrated the ability of a coupled thermal/mechanical DEM model to realistically model the formation of radial cracks in nuclear fuel during an initial power-up. Figure 2(a) shows the crack patterns predicted by the DEM model. In addition, an initial implementation of peridynamics was developed in MOOSE/BISON and demonstrated on a two-dimensional fuel fracture simulation, as shown in Figure 2(b).

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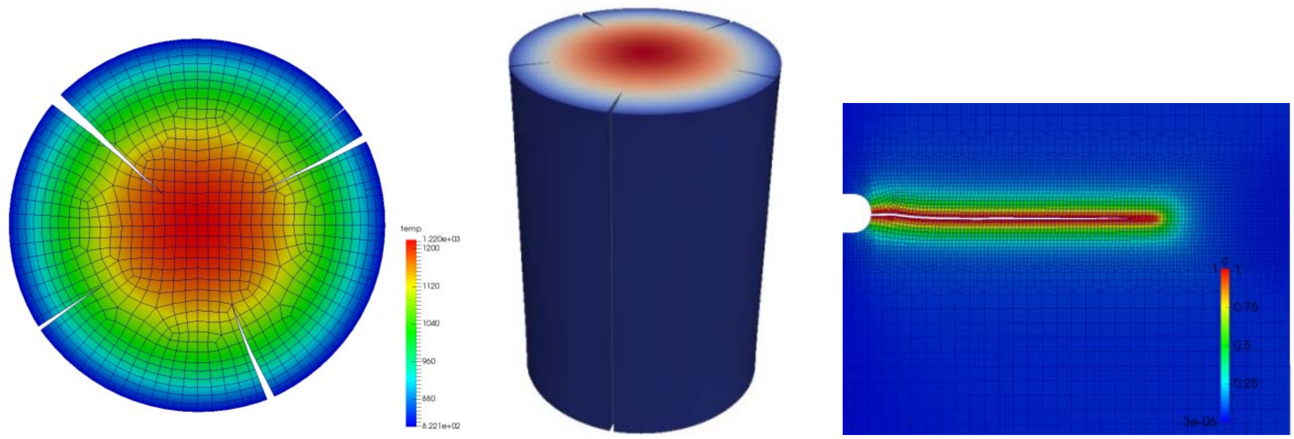
[1] Duke University

[2] C. L. Richardson, J. Hegemann, E. Sifakis, J. Hellrung, and J. M. Teran, "An XFEM method for modeling geometrically elaborate crack propagation in brittle materials," *International Journal for Numerical Methods in Engineering*, Vol. 88, No. 10, pp. 1042–1065, December 2011.

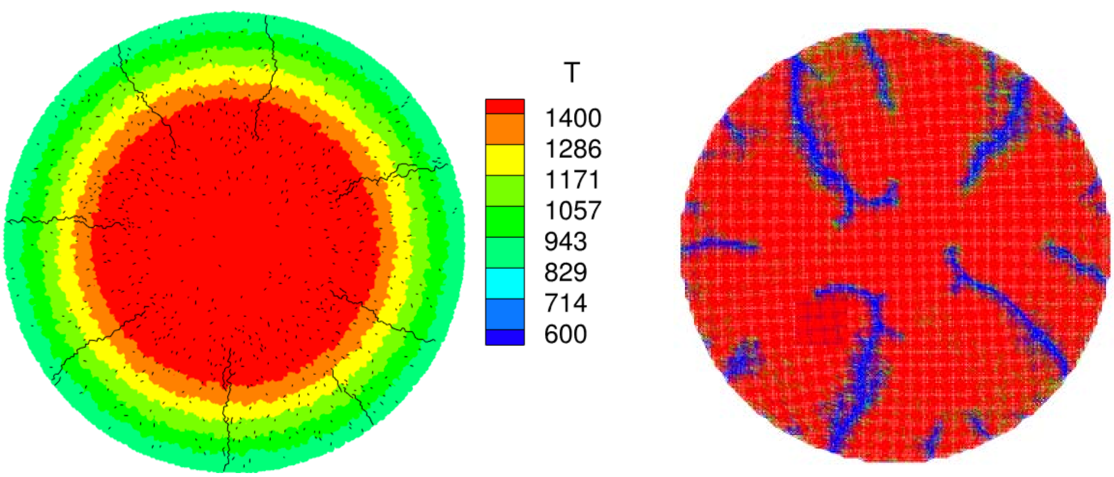


(a) Two dimensional fuel simulation with propagating cracks

(b) Three-dimensional fuel simulation with prescribed stationary cracks

(c) Demonstration of XFEM discontinuities inserted behind propagating phase field fracture

Figure 1. Results from MOOSE/BISON fracture simulations using XFEM.



(a) DEM simulation of fuel fracture, showing temperature contours

(b) Peridynamic simulation of fuel fracture, with failed bonds shown in blue

Figure 2. Results of 2D DEM and peridynamics simulations of a ceramic fuel pellet.

Benefits to DOE

This project has demonstrated improved capabilities for fracture modeling in nuclear fuel. This will provide a stronger basis for predictive simulation of fuel designs and postulated accident scenarios that are outside the realm of applicability of methods currently in use. The fracture modeling techniques developed in this work are also directly applicable to modeling fracture in other nuclear power plant components, such as reactor pressure vessels and containment vessels. This will improve the safety and efficiency of nuclear power generation. This project has already generated follow-on funding from the Consortium for Advanced Simulation of Light Water Reactors and the Light Water Reactor Sustainability Program.

Publications

Huang, H., B. Spencer, and J. Hales, “Discrete Element Method for Simulation of Early-Life Thermal Fracturing Behavior in Ceramic Nuclear Fuel Pellets,” *Nuclear Engineering and Design*, Vol. 278, pp. 515–528, October 2014.

Zhang, Z., J. Dolbow, and B. Spencer, “A Strategy for Integration over Partial Elements without Remapping State Data,” in preparation.

Spencer, B., H. Huang, J. Dolbow, and J. Hales, “Discrete modeling of early-life thermal fracture in ceramic nuclear fuel,” *Proceedings of WRFPM 2014*, Paper 100061, Sendai, Japan, September 14-17, 2014.

Presentations

Spencer, B., H. Huang, J. Dolbow, Z. Zhang, G. Pastore, and J. Hales, “Discrete modeling methods for fracture in ceramic nuclear fuel,” Halden LOCA Workshop, Aix-en-Provence, France, May 2015.

Spencer, B., Z. Zhang, and J. Dolbow, “Extended finite element method in multiphysics nuclear fuel simulations,” 13th US National Congress on Computational Mechanics, USNCCM12, San Diego, California, July 2015.

13-092—Fission Product Standard Production

Jana Pfeiffer, Kevin Carney, Christopher McGrath,[1] Martha Finck, and Mathew Snow

The global national security community needs fission product standards to support nuclear nonproliferation, counterproliferation, and forensics capabilities. Traditionally, the production of isotopes used to develop fast-fission product standards has required irradiation of significant quantities of fissionable material in a reactor capable of producing a fast spectrum. Cf-252 spontaneous fission decay results in a fission yield curve that is similar to the U-235 spectrum, with the highest probability of generated fission products shifted toward higher masses (Figure 1). Of particular interest, the probability of producing masses in the low-yield “valley” and “wing” regions of U-235 fission is significantly higher with Cf-252 spontaneous fission. Successful collection of Cf-252 particulate fission products, followed by isolation of desired isotopes via chromatographic separation, is an efficient, cost-effective, and safe method to produce fast-fission product standards.

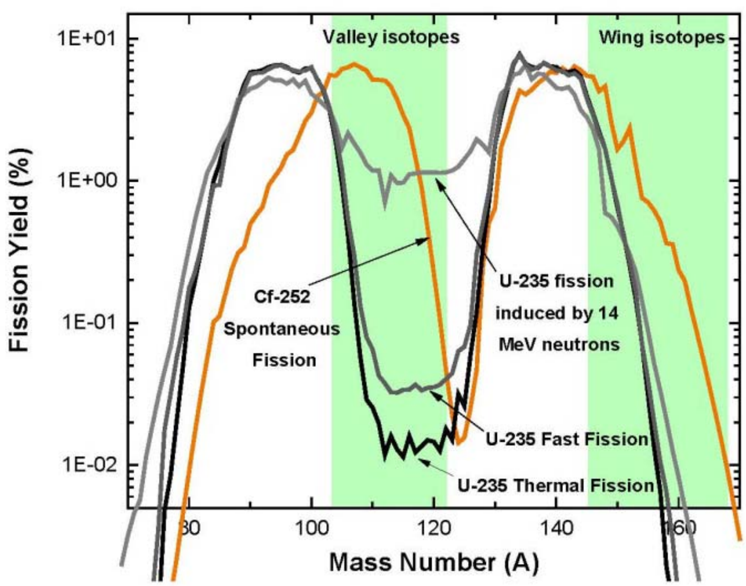


Figure 1. Comparison of U-235 and Cf-252 fission yields.

Summary

This effort was focused on collection and separation of lanthanide fission products. To this end, a literature search identified an isocratic high-performance liquid chromatography anion-exchange separation using a Dionex AS9-HC column and ethylenediaminetetraacetic acid (EDTA) as both the complexant and eluent. Lanthanide separation behavior of this system was characterized using nonradioactive surrogate solutions containing the elements yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, and dysprosium. Initial tests were performed by injecting 0.25 mL of a solution containing 50 µg of each analyte in 2% nitric acid. The 5-µmol EDTA eluent was adjusted to various pH levels (5, 6.5, 8, and 9). Comparison of the results of this testing identified the preferred eluent/complexant as EDTA adjusted to pH 6.5. In a second test, the 50-µg surrogate solution was injected in triplicate to provide statistics regarding purity and yield of the separated elements (Table 1). A third test was designed to verify the successful performance of this separation

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system at the expected lower concentrations of analytes that would be expected from the mass of Cf-252 that was available for this work.

Table 1. Purity and yield of selected elution fractions.

Element	Fraction	Purity	Yield
		(%)	(%)
Yttrium	5	100 ± 0	99 ± 0.28
Lanthanum	7	54 ± 1.4	92 ± 2.9
Cerium	11	98 ± 0.85	90 ± 1.3
Praseodymium	14	90 ± 0.51	74 ± 1.2
Neodymium	17	99 ± 0.10	90 ± 0.27
Samarium	24	97 ± 0.20	50 ± 3.2
Europium	22	100 ± 0.24	66 ± 7.6
Gadolinium	18	93 ± 1.5	58 ± 8.3
Terbium	12	96 ± 0.11	94 ± 0.49
Dysprosium	8	77 ± 6.0	22 ± 10

The spontaneous fission of Cf-252 generates measureable quantities of isotopes ranging from approximately 80 to 170 amu. CMPO (1 M octyl (phenyl phosphine oxide)-N,N-diisobutylcarbamoyl-methylphosphine oxide) was developed to extract trivalent and tetravalent transuranic and lanthanide isotopes as a group from highly acidic nuclear waste solutions. Eichrom Technologies' extraction chromatography product, RE Resin (1M CMPO in tributyl phosphateon an inert polymer support), has been applied to the group separation of lanthanide elements. A surrogate solution containing 50 ng/mL strontium, zirconium, molybdenum, ruthenium, palladium, silver, cadmium, tellurium, and cesium, in addition to the lanthanide elements listed above, was made to simulate the expected fission product mix from Cf-252. One milliliter of this solution was separated using an RE Resin column, and the 1-mL fractions that were collected were analyzed via inductively coupled plasma mass spectrometry. This test demonstrated that lanthanide elements could be quantitatively separated from the remaining constituents of the surrogate solution.

The Cf-252 source used to provide particulate fission products is installed in a fixture that is also used to collect gaseous fission products. A thin, 1-in. platinum disk with approximately 2.75 µm of electroplated Cf-252 is contained in a stainless-steel source holder. The Cf-252 source is covered with very thin nickel foil, which acts to contain any Cf-252 or Cm-248 daughter product material, while allowing smaller beta particulate and gaseous fission products to pass through. A metallic foil was placed in the holder approximately 1/4 in. above the source and then left in place for a period of time. The collection and purification cycle was performed twice; collection time for the first cycle was 19 days (456.17 hours), and collection time for the second cycle was 13 days (309.75 hours). Upon removal from the source holder, the foil was analyzed via gamma spectroscopy. The foil was leached in 3 M nitric acid, heat controlled to maintain the solution just below boiling, for approximately 2 hours. The leach solution and foil were analyzed via gamma spectroscopy. The leach solution was evaporated to near dryness, and sample constituents were brought back into solution with 1 mL of 3 M nitric acid. This solution was introduced to a column containing Eichrom RE Resin to separate the lanthanide fission products from other sample constituents. The solution collected from this preparatory separation was evaporated, and then 0.5 mL of 5 mmol EDTA was used to bring the lanthanide fission products back into solution. One-fourth of a milliliter of this solution was injected onto the high-performance liquid chromatography column, and 30 1-mL fractions of 5 mmol EDTA eluent were collected and analyzed via gamma spectroscopy.

Figure 2 compares the results of the gamma spectroscopy analysis of the fractions from the separation of the Cf-252 fission product solution to the results from inductively coupled plasma mass spectrometry analysis of the nonradioactive surrogate fractions. Two conclusions can be drawn from these data. This method successfully allows for collection and purification of quantities of lanthanide fission products within the detection limits of gamma spectroscopy equipment. Furthermore, the represented lanthanide fission products were successfully isolated from a solution containing fission products over the entire mass range of the Cf-252 probability curve (Figure 1). As seen in Figure 2, the detectable lanthanide fission products were found in the separation fractions that were predicted by the surrogate characterization of this separation protocol. Isotopes of gadolinium, terbium, and dysprosium were not observed within the detection limits of this analysis, so they are not represented in Figure 2. The lower predicted fission yields (0.02–0.3%) for the masses of these isotopes (159–166), compared to 5.96% for La-140, are one explanation for their absence. Improving future efforts by increasing fission product collection times, reducing time between collection of fission products and final analysis of the separated fractions, and increasing count times for fractions containing smaller quantities of fission products should result in successful collection of purified fractions of the higher mass lanthanides.

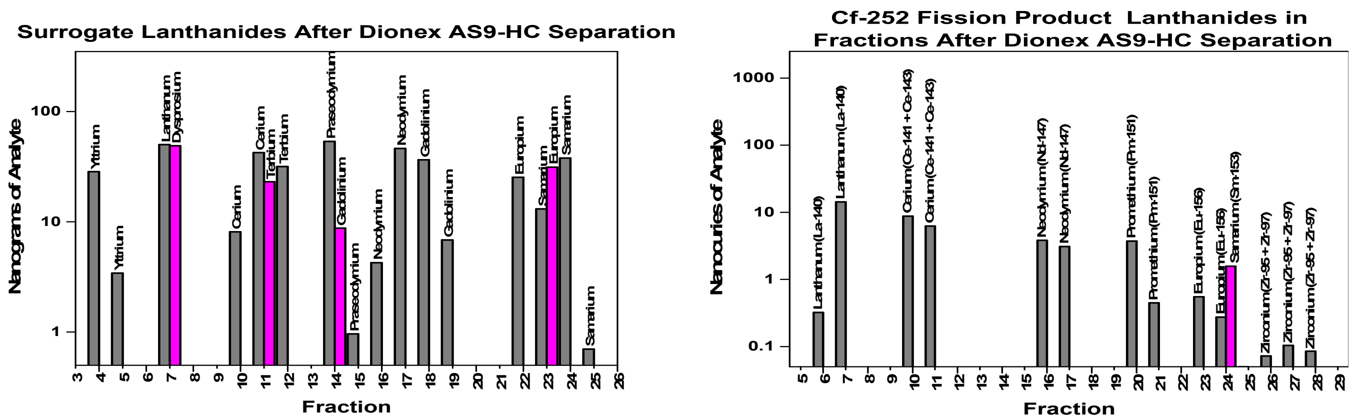

Figure 2. Comparison of analytes in fractions from surrogate versus Cf-252 fission product separation.

Benefits to DOE

Successful collection and separation of fission products from the spontaneous fission of Cf-252 supports DOE objectives to expand scientific knowledge and laboratory capabilities to conduct research and develop technology solutions for arms control and treaty verification. Capabilities developed may expand the suite of pure isotopes that can be provided for the Comprehensive Test Ban Treaty and National Nuclear Technical Forensics communities. This work will also support the Federal Bureau of Investigation in domestic post-detonation ground debris collection.

Presentations

Pfeiffer, J. K., C. A. McGrath, and K. P. Carney, "Fission Product Collection and Purification from the Spontaneous Fission of Cf-252," International Conference on Methods and Applications of Radioanalytical Chemistry (MARC X), American Nuclear Society, Kailua-Kona, Hawaii, April 2015.

13-095—Development and Validation of a Societal Risk Goal for Nuclear Power Plant Safety

Robert Youngblood, Michael Corradini, and Vicki Bier

Existing safety goals for commercial nuclear power plants are focused on radiological consequences to individuals rather than societal consequences and do not address the adverse effects of human relocation for indefinite periods. Such a goal structure does not fully reflect the range of reactor accident consequences that need to be avoided. Even a large release of radioactive material that causes a large number of people to be evacuated could have negligible health effects, but this does not mean it would cause negligible societal disruption. Among other things, a goal structure should arguably address collective dose and societal disruption. This project has evaluated the social disruption effects from severe reactor accidents as a basis for developing a societal risk goal for nuclear power plants. The project has studied the possible societal disruptions that could occur from nuclear power accidents, considering both past accidents and potential future accident scenarios, while also examining both the dose consequences and the number of people that would need to be evacuated in the event of a severe accident. The number of people to be evacuated appears to be a good proxy for the level of societal disruption from an accident while still being relatively straightforward to compute in an objective manner, and health effects and evacuation trade off directly against each other.

Summary

To inform the development of a useful goal structure, offsite impacts were quantified from selected severe reactor accidents at several plants on 24 different dates over a period of two years (2011 and 2012) using actual site-specific weather data. The plants chosen include high- and low-population sites. Using RASCAL, the number of people relocated was quantified for timeframes of four days, one year, two years, and 50 years after the accident and at various thresholds for relocation (0.5 rem through 4 rem). Ultimately, the results one year after an accident were selected as being representative of the greatest societal disruption. (Being relocated for only four days is not too disruptive if people are able to move back soon afterward; if relocation continues much longer than one year, many people will have settled into a "new normal" and no longer experience ongoing disruption.)

Also studied were the effects of different protective action thresholds for relocation. Lower thresholds result in fewer cancer fatalities but relocation of more people, while higher thresholds result in fewer people relocated at the expense of more cancer fatalities. The tradeoff between cancer fatalities and relocation (i.e., roughly how many people would need to be relocated to prevent one cancer fatality) was able to be quantified. Although results vary somewhat by location and accident scenario, to an order of magnitude, roughly 1,000 people would need to be relocated for each cancer fatality prevented. (Note that this result is based on the "linear no-threshold" dose response model.)

Different forms for quantifying the combined impact of cancer fatalities and relocation were evaluated. The sensitivity analysis includes parameters such as how much weight to give to fatalities versus relocation, whether to incorporate risk aversion with respect to large numbers of people relocated, and whether there are interaction effects (e.g., whether avoiding large numbers of cancer fatalities is considered more important following a large relocation than following a small relocation).

Based on this work, it is proposed that a reasonably practicable societal safety goal would be a weighted sum of expected cancer fatalities and expected population relocation (weighted to reflect the relative importance of dose versus relocation). Such a goal would, of course, depend on the setting of protective action guidelines. Satisfaction of such a goal would imply that even a severe accident would not result in either an extremely large number of cancer fatalities or a massive relocation, but some flexibility in how to meet such a goal exists. Currently, for two reasons, no specific numerical weighting factor is proposed for representing the relative importance of relocations versus cancer fatalities. First, this is fundamentally (and appropriately) a policy judgment. Moreover, work being done under funding from other agencies is currently quantifying the economic losses that could be expected due to severe nuclear accidents in the United States. Those results, once final, could be useful in quantifying the required weighting factor (e.g., using the criterion of $2,000 per person-rem in NUREG/BR-0058, "Regulatory Analysis Guidelines of the U.S. Nuclear Regulatory Commission" [2004]). Additionally, even without revision of the existing safety goals, the current thinking could be applied to the safety-goal-based screening process specified in NUREG/BR-0058.

One student participating in the project has completed his Ph.D. and is currently on faculty at the Air Force Institute of Technology. He is continuing to collaborate with the project. Also collaborating on the project were a number of individuals active in emergency planning at the U.S. Nuclear Regulatory Commission, and they participated in an INL-sponsored workshop on assessment of the risk of extreme floods to pursue commonalities in the assessment and management of severe accidents.

Benefits to DOE

The work has already generated insights into possible improvements in evacuation policy for large accidents (e.g., by extending emergency planning zones beyond 10 miles if needed). Similar methods (using state-of-the-art dispersion models and geographic information systems) should be applicable to emergency planning in other areas as well (chemical emergencies, military planning, etc.). The results of this work could be applied to illustrate the benefits of novel reactor technologies and thereby help to build public support for appropriate deployment of new nuclear plants in the aftermath of the events at Fukushima, Japan. Better modeling of societal disruption (rather than relying on relatively crude proxies, such as number of fatalities) is a particularly novel aspect of the work.

Publications

Bier, V., M. Corradini, R. Youngblood, C. Roh, and S, Liu, "Development of an Updated Societal Risk Goal for Nuclear Power Safety," *Proceedings of Probabilistic Safety Assessment and Management*, Honolulu, Hawaii, June 22–27, 2014.

Roh, C, R. Youngblood, M. Corradini, V. Bier, and S. Liu, "Development of a Societal-Risk Goal for Nuclear Power Safety," *Proceedings of the 16th International Topical Meeting on Nuclear Reactor Thermalhydraulics (NURETH-16)*, August 30–September 4, Chicago, Illinois.

Presentations

Roh, C., V. M. Bier, M. Corradini, and S. Liu, "Development of an updated societal-risk goal for nuclear power safety," Society for Risk Analysis, Denver, Colorado, December 2014.

13-097—MOOSE Capability Extension in Support of Full-Core Modeling

Derek Gaston, Cody Permann, David Andrs, John Peterson, and Andrew Slaughter

Nuclear reactor operation is inherently a multiscale, multiphysics phenomenon. Large-scale physics such as fluid flow and heat conduction are driven by atomistic effects of the fission process. Simulation of such a complex system is a daunting task. This project aims to add fundamental capabilities to the INL's computer simulation framework known as MOOSE in support of multiscale nuclear reactor modeling. The main objectives center around three capabilities:

- Link applications
- Deliver tools to the community
- Provide a stable platform ensuring these complex capabilities can be easily developed and maintained.

Summary

This LDRD project has seen immense success over the duration of its lifetime. During the first year of the project, advanced technical capability was added to the MOOSE multiphysics platform, enabling first-of-a-kind, full-core, multiscale nuclear reactor simulations by efficiently linking multiple MOOSE-based applications. That capability has been a showcase for the direction INL has taken for modeling and simulation.

The second year of the project was highlighted by large advances in software engineering practices to accelerate development of full-core simulation capabilities. In March 2014, MOOSE was released as open-source software, which has led to a rapid increase in both the number of users and the number of developers of MOOSE. MOOSEBuild, a new tool for coordinating development of multiple, interdependent MOOSE-based applications, was also created during the second year. A novel workflow for streamlining development of MOOSE-based applications was published in the proceedings of the Working towards Sustainable Software for Science: Practice and Experiences workshop. During the second year, the MOOSE project was also awarded an R&D 100 Award from *R&D Magazine*, in large part because of the full-core simulation capability developed during this LDRD.

The third year of the project was spent refining and improving the robustness of features added for full-core modeling. The Multiapps and Transfers systems in MOOSE have both undergone significant refactoring and cleanup, making those tools accessible to other projects. The Consortium for Advanced Simulation of Light Water Reactors project is now making extensive use of the Multiapps system for its virtual reactor project. New capabilities to dynamically link applications together on the fly have also been implemented, further enabling advanced multiapplication simulations. The Transfers system was made much more efficient, reducing the time needed to run all Multiapps simulations. Finally, the lessons learned from the original development of the tool, MOOSEBuild (the continuous integration testing utility), have been used to develop an improved second-generation tool currently called Civet, which can interact with more open-source tools, is more flexible for the main "git"-based projects hosted by INL, and contains an improved user interface. This tool will eventually be made open source and used for external scientific development workflows.

Benefits to DOE

This project has benefited several DOE missions. It directly benefits energy resources, because the capabilities produced are already being utilized to study advanced nuclear reactor and fuel concepts. The MOOSE platform is currently being leveraged extensively by both the Nuclear Engineering Advanced Modeling and Simulation and the Consortium for Advanced Simulation of Light Water Reactors programs. These capabilities are also impacting environmental quality and science. The intrinsic capabilities being developed are being applied to many disparate areas of environmental science and scientific endeavors (including fundamental material science studies).

Publications

Gaston, D., C. Permann, D. Andrs, and J. Peterson, "Massive Hybrid Parallelism for Fully Implicit Multiphysics," *Proceedings of the International Conference on Mathematics and Computational Methods Applied to Nuclear Science and Engineering*, Sun Valley, Idaho, May 5–9, 2013.

Gaston, D., J. Peterson, C. Permann, D. Andrs, A. Slaughter, and J. Miller, "Continuous Integration for Concurrent Computational Framework and Application Development," *Journal of Open Research Software*, Vol. 2, July 1–6, 2014.

Gaston, D. R., C. J. Permann, J. W. Peterson, A. E. Slaughter, D. Andrs, Y. Wang, M. P. Short, D. M. Perez, M. R. Tonks, J. Ortensi, and R. C. Martineau, "Physics-based multiscale coupling for full core nuclear reactor simulation," *Annals of Nuclear Energy, Special Issue on Multi-Physics Modelling of LWR Static and Transient Behaviour*, Vol. 84, pp. 45–54, October 2015.

Gaston, D., C. Permann, J. Peterson, A. Slaughter, D. Andrs, Y. Wang, M. Short, D. Perez, M. Tonks, J. Ortensi, and R. Martineau, "Physics Based Multiscale Coupling for Full Core Nuclear Reactor Simulation," *Annals of Nuclear Energy*, in press.

Mangeri, J., O. Heinonen, D. Karpeyev, and S. Nakhmanson, "Influence of elastic and surface strains on the optical properties of semi-conducting core-shell nanoparticles," *Physical Review Applied*, Vol. 4, No. 1, p. 014001 (10 pages), July 2015, http://dx.doi.org/10.1103/PhysRevApplied.4.014001.

Short, M., D. Gaston, C. Stanek, and S. Yip, "A Perspective on Coupled Multiscale Simulation and Validation in Nuclear Materials," *MRS Bulletin*, Vol. 39, pp. 71–77, 2014.

Slaughter, A., D. Gaston, J. Peterson, C. Permann, D. Andrs, and J. Miller, "Continuous Integration for Concurrent MOOSE Framework and Application Development on GitHub," *Workshop on Sustainable Software for Science: Practice and Experiences 2 (WSSSPE2)*, New Orleans, Louisiana, November 16, 2014.

Presentations

Gaston, D., C. Permann, D. Andrs, and J. Peterson, "Massive Hybrid Parallelism for Fully Implicit Multiphysics," SIAM Conference on Computational Science and Engineering, SIAM CS&E13, Boston, Massachusetts, February 25–March 1, 2013.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, et al., "Multiphysics, Multiscale Algorithms for Nuclear Power Applications," Plenary, International Conference on Mathematics and Computational Methods Applied to Nuclear Science and Engineering, Sun Valley, Idaho, May 5, 2013.

Gaston, D., C. Permann, D. Andrs, J. Peterson, and A. Slaughter, "MOOSE Workshop," Commonwealth Scientific and Industrial Research Organisation, Perth, Australia, June 11–13, 2013.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, et al., "Full Core Reactor Simulation Using MOOSE," Closing Plenary, American Nuclear Society GLOBAL 2013, Salt Lake City, Utah, September 29-October 3, 2013.

Gaston, D., C. Permann, D. Andrs, J. Peterson, and A. Slaughter, "MOOSE Workshop," Texas A&M University, College Station, Texas, October 29–31, 2013.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, and R. Martineau, "MOOSE: Multiphysics Object Oriented Simulation Environment," NASA Langley Research Center, Newport News, Virginia, January 2014, invited presentation.

Gaston, D., C. Permann, D. Andrs, J. Peterson, and A. Slaughter, "Physics Based Coupling for Multiscale Full Core Nuclear Reactor Simulation," SIAM Conference on Parallel Processing for Scientific Computing, SIAM PP14, Portland, Oregon, February 18–21, 2014.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, and R. Martineau, "MOOSE: Multiphysics Object Oriented Simulation Environment," EPRI Safety Technology Week, Charlotte, North Carolina, June 2014.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, and R. Martineau, "Simplifying Multiphysics through Application Composition," 20 Years of Computational Science with PETSc, Lemont, Illinois, June 2015.

Gaston, D., C. Permann, D. Andrs, J. Peterson, A. Slaughter, and R. Martineau, "MOOSE Workshop (invited)," Scientific Software Development Short Course, Urbana, Illinois, July 2015.

Permann, C., D. Gaston. D. Andrs, J. Peterson, A. Slaughter, and R. Martineau, "MOOSE Tutorial," 20 Years of Computational Science with PETSc, Lemont, Illinois, June 2015.

13-105—Micro/Nano Scale AFM-Based Thermal Conductivity Measurement and Atomistic Modeling for Oxide Fuel: The Effects of Grain Boundary, Fission Gas, and Radiation Damage

Jian Gan, Xianming "David" Bai, Yong Yang,[1] Heng Ban,[2] and Aleksandr Chernatynskiy[1]

This research effort studies the microstructure and radiation effects on the thermal conductivity of oxide fuel using a novel measurement technique and complementary computer modeling. By using a bottom-up approach, the effects of tailored microstructures and controlled radiation damage on materials' thermal conductivity can be individually evaluated and modeled. The complementary atomistic modeling of the thermal transport is conducted to compare the results directly with experiments. Specifically, the following objectives are to be accomplished: (a) determine grain boundary (GB) thermal resistance for different types of GBs in undamaged materials to investigate how specific GB structure affects the thermal transport; (b) investigate the thermal resistance of GBs with fission-gas implantation by considering that different GBs may have different effects on fission-gas segregation; and (c) determine thermal conductivity degradation at different irradiation temperatures.

Summary

A comprehensive investigation of the Kapitza resistance in CeO_2 as a function of GB-type (twist or tilt) orientation (001, 011, or 111) and misorientation angles was successfully conducted and analyzed with the help of the extended Read-Shockley model. This resulted in the simple expression of the GB Kapitza resistance as a function of the misorientation angle. A publication presenting the results of this effort has been submitted to the *International Journal of Heat and Mass Transfer*. The effect of defect segregation at GBs on thermal transport was further elucidated. Two types of defects are considered: (a) off-stoichiometry at GB in CeO_2 and (b) krypton atoms deposition/accumulation near the GB. For the former, oxygen vacancies were created at GBs to study how oxygen-deficit GBs in CeO_{2-x} affect the thermal resistance. The GB thermal resistance increases almost linearly with the local off-stoichiometry. The atomistic results were then input to an analytical model to evaluate the effects of segregation of oxygen vacancies on thermal transport at realistic length scales. The segregation of oxygen vacancies were found to improve the thermal transport, especially when the grain size is less than 400 nm. The results may explain why nanograined, high-burnup structures have improved thermal conductivity once they form. For the latter, potential of the Buckingham form has been developed for the Kr-CeO_2 interactions on the basis of the ab-initio database. The effect of different concentrations of krypton atoms was studied for three different GBs. The results of this investigation are consistent with the data obtained from the off-stoichiometries studies, in that the Kapitza resistance of the defective GBs increases with the concentration of the defects. Moreover, the relative difference in Kapitza resistance of different GBs is significantly reduced in defective GBs and approaches the same value for all GBs as the amount of defects increases. This result is consistent with the prediction of the Diffuse Mismatch Model, which for fully diffusive scattering at the interface predicts the same Kapitza resistance for all types of GBs.

To study the stoichiometry effects on CeO_2 thermal conductivity, off-stoichiometric pellets were prepared by annealing the sintered stoichiometric CeO_2 pellets in a 4% H_2/N_2 gas mixture for 24 hours at temperatures of 450, 650, 850 and 1,050°C. The electronic structure of annealed CeO_{2-x} was characterized by using x-ray photon spectroscopy (XPS). Figure 1(a) shows three-dimensional, core-level XPS spectra for both stoichiometric and 850°C annealed non-stoichiometric ceria. In the stoichiometric ceria, the spectra consist of six peaks (U, U", U'", V, V", and V'") corresponding to the electronic state of Ce^{4+}. Two new peaks (U' and V') were found in the spectra of off-stoichiometric ceria. The oxygen/ceria ratio of an 850°C annealed ceria pellet was measured as 1.88

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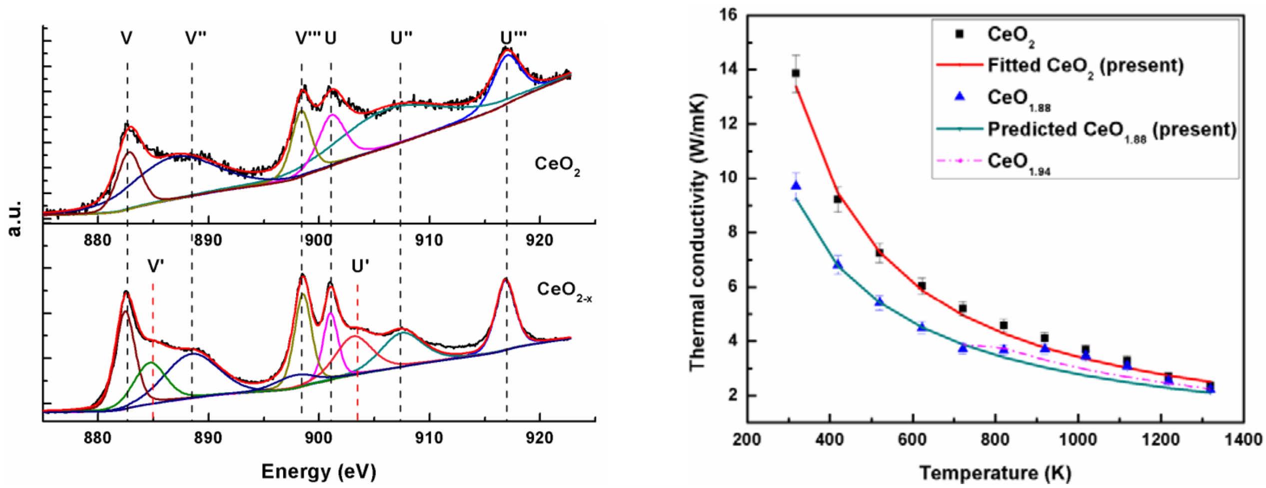
by using an inductively coupled plasma mass spectrometry and combustion technique. The thermal diffusivities of off-stoichiometric ceria are measured by using the laser flash analysis technique, and the thermal conductivities were calculated from measured values of thermal diffusivity, with the additional knowledge of specific heat capacity and density. The analytical calculations are based on Callaway's relaxation time approximation and generalized gradient approximation phonon dispersion spectra by considering the anisotropy of thermal conduction in polycrystalline.



(a) (b)

Figure 1. XPS of ceria (a) and thermal conductivity data for CeO_2, $CeO_{1.88}$, and $CeO_{1.94}$ (b).

This experiment indicates a significant reduction of thermal conductivity of ceria with reduced oxygen/ceria ratio. In certain low-oxygen environments, the oxygen vacancy concentration increases with annealing temperature. Modeling efforts to calculate the thermal conductivity of ceria produce results that agree well with the experimental measurement at a low-temperature region (<773 K). The discrepancy at temperature between 773 and 1,223 K can be explained as a combined result of increasing electron contribution to thermal transport and stoichiometry change during laser flash analysis. This study demonstrates the capability of predicting the thermal conductivity of off-stoichiometric ceria by implementing the vacancy concentration factor x in the model.

A thermal-resistance measurement approach based on the frequency-scan photothermal-reflectance technique was developed. The approach is capable of extracting the thermal resistance of a vertical interface that is embedded in a homogenous and isotropic material, which provides a reference to the measurement that is based on the spatial-scan photothermal-reflectance technique. Additionally, the thermal resistance of an artificial interface was measured on a silicon-bonding sample. The results of the frequency-scan and spatial-scan measurements agree well with each other. Finally, using the spatial-scan approach, the GB thermal resistances of the CeO_2 sample were measured in the range of 8×10^{-9} m^2K/W to 8×10^{-7} m^2K/W at different GBs. Similarly, local thermal diffusivity of the CeO_2 sample was also found to vary in the range of 2×10^{-6} m^2/s to 6×10^{-6} m^2/s in different grains.

Benefits to DOE

Light-water reactor parameters, such as nominal power level and fuel temperature margin to failure, have been limited by the poor thermal conductivity of oxide fuel and the resulting large temperature gradient. A better understanding of the thermal conductivity of oxide fuel during operation will have a significant impact on developing advanced light-water reactor fuels with improved thermal physical properties that can enhance the safety and performance of commercial nuclear fuels. The fundamental study will also contribute to DOE's leading role on basic science research of materials' behavior and performance in extreme environments.

Publications

Wu, Y., and Y. Yang, "Evaluate the Thermal Conductivity of Off-Stoichiometry Cerium Oxide," 2015 American Nuclear Society Winter Meeting, accepted.

Wu, Yuedong, Mehrad Mehr, Juan C. Nino, Aleksandr Chernatynskiy, and Yong Yang, "Experimentally and Analytically Evaluate the Thermal Conductivity of Non-stoichiometry Ceria," *Applied Physics Letters*, submitted.

Zheng, Z., X. Chen, B. Deng, A. Chernatynskiy, S. Yang, L. Xiong, and Y. Chen, "Phonon Thermal Transport through Tilt Grain Boundaries in Strontium Titanate," *Journal of Applied Physics*, Vol. 116, 2014.

Presentations

Bai, X., A. Chernatynskiy, and J. Gan, "Misorientation-Dependence of Grain Boundary Thermal Resistance in CeO_2," 2014 TMS Annual Meeting, San Diego, California, February 2014.

Bai, X., A. Chernatynskiy, and J. Gan, "Effects of Misorientation, Temperature, and Stoichiometry on Grain Boundary Thermal Resistance in CeO_2," 2014 Nuclear Materials Conference (NuMat2014), Clearwater, Florida, October 2014.

Chernatynskiy, A., X. Bai, and J. Gan, "Kapitza Resistance of the Grain Boundaries in Ceria (poster)," 2014 ANS Meeting, Reno, Nevada, June 15–19, 2014.

Chernatynskiy, A., X. Bai, and J. Gan, "Thermal Boundary Resistance and Irradiation Effects of the Grain Boundaries in Ceria," 2015 TMS Meeting, Orlando, Florida, March 15–19, 2015.

Wu, Y., H. Ban, X. Bai, A. Chernatynskiy, J. Gan, and Y. Yang, "Correlation between Thermal Conductivity and Microstructural Evolutions in CeO_2 Upon Radiation and Fission Gas Implantation," 2014 TMS Symposium: Radiation Effects in Oxide Ceramics and Novel LWR Fuels, San Diego, California, February 16–20, 2014.

13-106—Building Organic-Inorganic Hybrid Materials to Protect Metal Ion Sequestering Agents from Radiation-Induced Oxidative Damage

Peter Zalupski, Bruce Mincher, Michael Schultz,[1] and Gary Buettner[1]

Radiolytic damage incurred to solvent extraction reagents during the process of hydrometallurgical recovery of actinides from used nuclear fuel has obstructed aqueous separations for decades. This project supports the back end of the nuclear fuel cycle through studies of the "shielding" properties of mesoporous carbon nanostructures, which will be utilized as encapsulating hosts for the metal-ion complexing reagents. The mesoporous carbon (host)-complexant (guest) hybrid materials are tested for their ability to alleviate the damaging influence of free radicals produced when the energy of radioactive decay is deposited in matter. The project seeks antioxidizing benefits of such hybrid capsules.

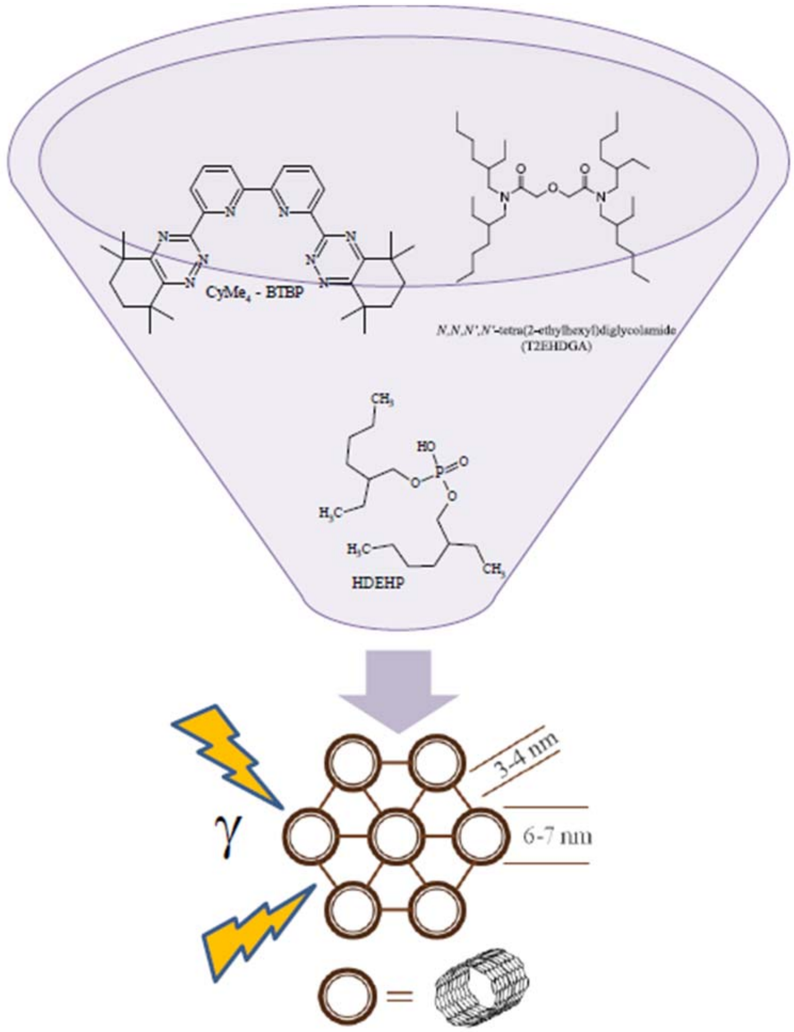


Figure 1. Graphical connotation of the proposed radioprotection concept. Hybrids shielding the pictured molecules from gamma radiation were successfully prepared and tested.

Summary

Studies in FY 2013 proved the scientific concept proposed in this LDRD project. The metal-ion coordination properties, when compared for the "protected" system (hybrid) and "unprotected" system (reagent in solvent), revealed the antioxidizing benefit of the shielding mesoporous capsule. Studies in FY 2014 further substantiated the "radioprotection" concept by translating the results onto a very different molecular platform relative to the original chemistry. A hybrid system where an organic reagent is nitrogen heterocyclic structure was successfully prepared and tested. In FY 2015, the final validation was performed for a third class of metal-ion complexing compounds. Figure 1 shows the structures of all reagents used to build the hybrid separation systems to illustrate the proposed concept. Figure 2 illustrates the concept development, showing the overall encapsulation idea and testing results for the hybrid containing a phosphoric acid-type complexing agent.

This LDRD supported the graduate studies of two students from the University of Iowa.

[1] University of Iowa

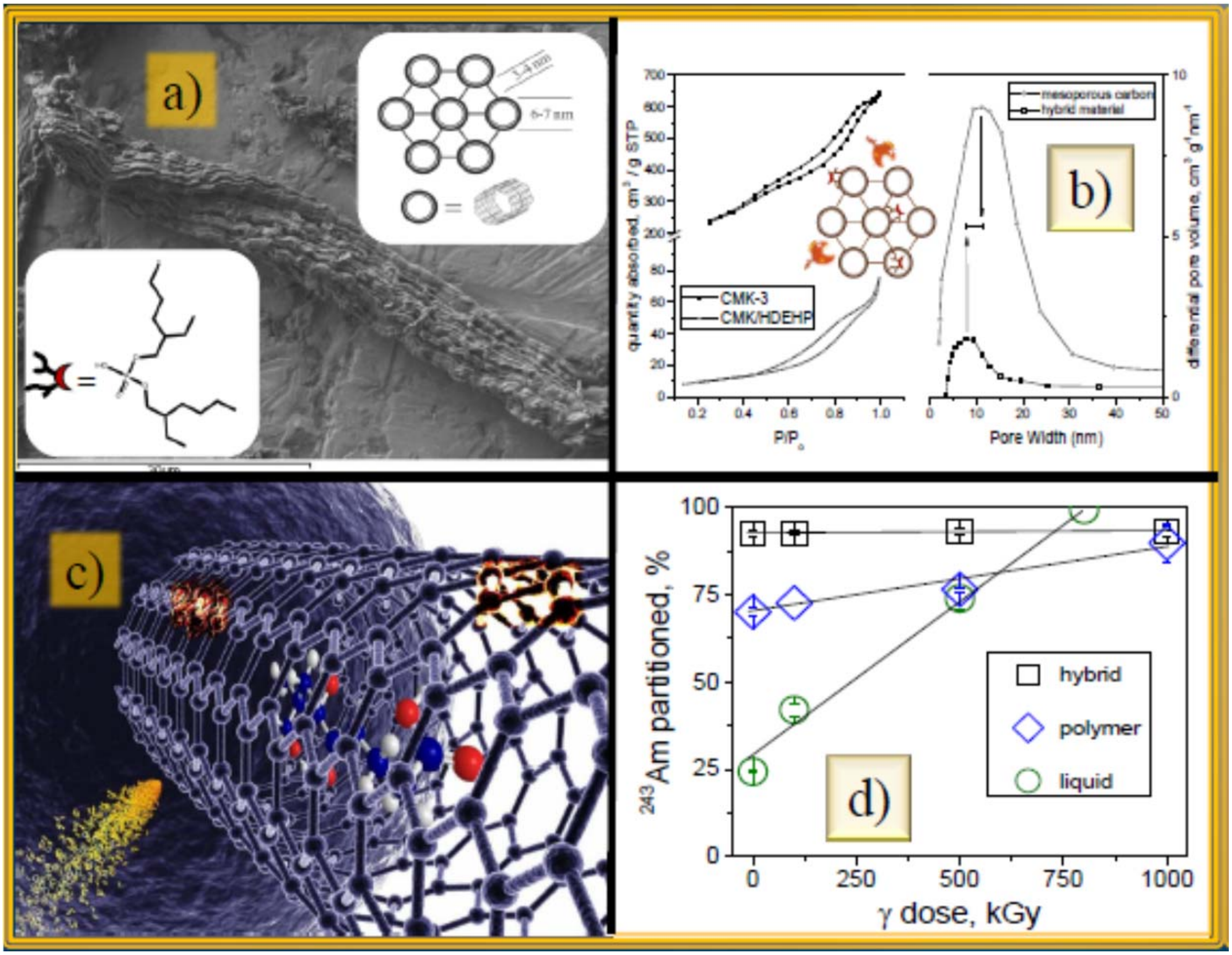


Figure 2. Radiation-resistant hybrid materials concept development: (a) scanning electron microscope micrograph of mesoporous carbon loaded with organophosphorus reagent, (b) analyses of N_2 adsorption/desorption isotherms that suggest reagent has entered the porous structure of carbon, (c) graphical representation of radiolytic protection concept, and (d) comparison of γ-induced degradation effects on the studied (protected and unprotected) systems.

Benefits to DOE

This LDRD will broaden INL's participation in the vastly expanding field of material science. The field of organic-inorganic supramolecular assembly has a variety of applications, one of which is advancement in the area of hydrometallurgical recovery of valuable materials from various aqueous streams. Development of mesoporous radioprotectants offers an innovative spin on aqueous recovery of actinides. A revolutionary advancement in the state of the art in the area of aqueous separations often calls for a complete redefinement of a separations concept. This concept offers an alternative by seeking to develop a revolutionary mechanism to preserve the already proven separation chemistry. This work will strengthen INL's mission to maintain leadership in the area of fuel-cycle development R&D. The collaboration with the University of Iowa establishes a valuable connection with our nation's newest graduate program in the field of radiochemistry.

Publications

"Adsorption Properties of Protactinium on the Surfaces of Mesoporous Carbon," *Radiochimica Acta*, in preparation for submission.

"Encapsulation of Ion-Sequestering Agents in Mesoporous Carbon to Reduce Radiation-Induced Oxidative Damage," *Journal of Inorganic Chemistry,* in preparation for submission.

Presentations

Multiple presentations at the Actinide Separations Conference, Separations Science and Technology Conference, Americian Chemical Society (National and Regional), and 1st SACSESS International Workshop.

13-115—Multi-Scale Full-Core Reactor Physics Simulation of the Advanced Test Reactor

Mark DeHart, Yaqi Wang, Kord Smith,[1] Jim Morel,[2] Cristian Rabiti, Hongbin Zhang, Richard Martineau, and Barry Ganapol[3]

Historically, experiments have been performed to understand fuel performance and for all aspects of fuel design; the 52 reactors built at INL since 1949 are a testament to that history. In today's budget-restricted environment, the cost of data acquisition through experimental testing severely limits the design and construction of experimental reactors and even measurements in existing reactors. However, such data are still needed to improve reactor design and provide the ability to advance the state of the art. Hence, it is necessary to develop alternate tools that can be used to test the potential feasibility of design concepts before proceeding with fabrication. The concept of a virtual reactor provides such a capability and provides the means to substantially reduce the cost of experimentation by allowing virtual experiments before any hardware development is initiated. Because the ATR is designed to drive a wide range of experimental phenomena, it is the perfect vehicle for demonstration of the concept of a virtual reactor. The objective of this research is to develop a prototypic, multiscale, multiphysics virtual reactor based on ATR. Specifically, the research team is working to develop a neutron transport solver with Rattlesnake, which is a neutron transport application built on INL's MOOSE framework. In this research, a three-scale solution is proposed: fuel-resolved, plate-homogenized, and element-homogenized scales. This approach allows the user to focus computational effort on the region of the core that is of most interest while still providing coupling to other regions of the core that affect the region of interest. This multiscale approach will make a full, three-dimensional virtual reactor model tractable on existing computational platforms. The resulting capability is to be used to support the mission of performance improvements together with continued safe and productive operation of the ATR. In addition, the technology developed during this project will ultimately be of value for support of the existing fleet of experimental and power reactors and to assist in the design of future reactor types.

Summary

Multiple scales require multiple levels of resolutions corresponding to different discretization schemes. Rattlesnake currently solves the radiation transport equation in the self-adjoint angular flux (SAAF) formulation discretized with a multigroup approximation in energy, a continuous finite element method (CFEM) in space, and a discrete ordinates (SN) approximation in angle. In FY 2013, two new transport schemes were developed: the spherical harmonics expansion method (PN) and the least-squares method with CFEM and SN.

In FY 2014, the primary objective of this work was to develop and implement interface conditions for coupling scales on separate subdomains on which different solution schemes may simultaneously apply, including different angular solutions using S_n or P_n, a varying number of energy groups, and different levels of spatial resolution. Several objectives have been accomplished: (a) development of an unstructured mesh splitter; (b) development and implementation of Lagrange multipliers for the simple convection-collision equation applied to the neutron transport equation; and (c) initial implementation of a mortar finite element method framework within Rattlesnake. Actualization within Rattlesnake of methods based on the mortar finite element method required deployment of a mortar finite element method architecture within the MOOSE framework itself. This modification to MOOSE was completed, and initial work to apply this technology with Rattlesnake solution

[1] Massachusetts Institute of Technology

[2] Texas A&M University

[3] University of Arizona

algorithms was initiated. Progress in FY 2014 also included improvements to individual discretization schemes in Rattlesnake. Significant progress has been made through development of two individual high-order transport schemes: the LS-SN-CFEM method and the SAAF-PN-CFEM method.

During FY 2015, significant improvements have been made in Rattlesnake. For example, work was completed and verified to improve the performance of the nonlinear diffusion acceleration scheme when used to accelerate SAAF-SN-CFEM transport calculations. Implementation of a first-order version of the discrete ordinates approximation of the transport equation was completed using a discontinuous finite element method approach. Improvements were completed in least-squared finite element solutions. Finally, efforts focused on implementation of the multiscale transport capability in Rattlesnake. Progress on the latter was delayed by full implementation of support for a mortar finite element method capability in the MOOSE framework. This method was deemed to be most appropriate for meeting multiscale analysis needs. It was further determined that the mortar finite element method has significant potential for application in other MOOSE-based applications.

Because it has not been fully implemented in MOOSE, full three-dimensional ATR simulations with a multiscale approach were not completed by the end of the project. However, the approach has been demonstrated in two dimensions and has great potential for providing the three-dimensional simulations. Full implementation will continue to be pursued under FY 2016 funding for Transient Reactor Test (TREAT) modeling and simulation to support similar needs for TREAT transient modeling. An ATR mesh has been completed and will be used in revisiting multiscale ATR simulations once the approach has fully matured and been tested for TREAT.

Two doctoral students from the Massachusetts Institute of Technology and one doctoral student from Texas A&M University are participating in this project.

Benefits to DOE

These multiscale methods are laying the groundwork for next-generation, multiphysics analysis of ATR for improved performance, safety, and economics. This will, in turn, improve the efficacy of the ATR mission in support of Naval Reactors, DOE-NE, and National Nuclear Security Administration needs. Upon demonstration of the applicability of this approach to ATR, the technology could and should be extended to light-water reactors and next-generation reactor designs, consistent with DOE Office of Science and DOE-NE programs.

The TREAT Facility was not considered when this project began, but the facility has since been the location for multiphysics modeling and simulation. Although not the original intent, the work completed at the TREAT Facility has provided capabilities that allowed rapid deployment and testing of Rattlesnake for both steady-state and transient analysis. Multiscale capabilities will be key in allowing a low-order transport solution for the core power transient to be coupled with a high-order solution to simulate in detail the transient response of target experiments. This will assist in the design and post-irradiation study of fuel experiments. This work may be employed in early startup testing, at least to provide confirmatory analyses.

Publications

Gaston, D. R., C. J. Perman, J. W. Peterson, A. E. Slaughter, D. Andrs, Y. Wang, S. P. Short, D. D. Perez, M. R. Tonks, J. Ortensi, L. Zou, and R. C. Martineau, “Physics-based multiscale coupling for full core nuclear reactor simulation,” *Annals of Nuclear Energy,* Vol. 84, pp. 45–54, October 2015.

Hansen, J., J. Peterson, J. Morel, J. Ragusa, and Y. Wang, “A Least-Squares Transport Equation Compatible with Voids,” *Journal of Computational and Theoretical Transport*, Vol. 43, No. 1-7, September 2014

Schunert, S., Y. Wang, and R. C. Martineau, “A New Mathematical Adjoint for the Modified SAAF-SN Equations,” *Annals of Nuclear Energy,* Vol. 75, pp. 340–352, January 2015.

Presentations

Ortensi, J., M. Ellis, Y. Wang, H. R. Hammer, J. P. Senecal, F. N. Gleicher, S. Schunert, M. D. DeHart, K. S. Smith, and R. C. Martineau, "Solution of the Hot Zero Power BEAVRS Using a Pin-Cell Homogenized Model," ANS Winter Meeting 2015, American Nuclear Society, Washington D.C., November 8–12, 2015.

Schunert, S., Y. Wang, J. Ortensi, F. N. Gleicher, and M. D. DeHart, "A Flexible Nonlinear Diffusion Acceleration Method for the First Order Eigenvalue Sn Equations Discretized with Discontinuous FEM," PHYSOR 2016: Unifying Theory and Experiments in the 21st Century, American Nuclear Society, Sun Valley, Idaho, May 1–5, 2016, accepted.

Schunert, S., Y. Wang, M. D. DeHart, G. Youinou, and R. C. Martineau, "Unconditionally Stable Nonlinear Diffusion Acceleration for the 1st Order SN Equations," Idaho National Laboratory, Early Career Research Symposium, Idaho Falls, Idaho, July 30–31, 2015.

Schunert, S., Y. Wang, J. Ortensi, F. N. Gleicher, M. D. DeHart, and R. C. Martineau, "A High-Order Nonlinear Diffusion Acceleration for the S N Equations Discretized with the Discontinuous FEM: Fourier Analysis," ANS Winter Meeting 2015, American Nuclear Society, Washington D.C, November 8–12, 2015.

Wang, Y., M. D. DeHart, D. R. Gaston, F. N. Gleicher, R. C. Martineau, J. W. Peterson, and S. Schunert, "Convergence study of Rattlesnake solutions for the two-dimensional C5G7 MOX benchmark," MC2015 - Joint International Conference on Mathematics and Computation (M&C), Supercomputing in Nuclear Applications (SNA) and the Monte Carlo (MC) Method, American Nuclear Society, Nashville, Tennessee, April 19–23, 2015.

Wang, Y., S. Schunert, M. D. DeHart, and R. C. Martineau, "Hybrid PN-SN Calculations with SAAF for the Multiscale Transport Capability in Rattlesnake," PHYSOR 2016: Unifying Theory and Experiments in the 21st Century, American Nuclear Society, Sun Valley, Idaho, May 1–5, 2016, accepted.

13-121—Advanced In Situ Measurement Techniques in TREAT

J. Keith Jewell, Tony Hill, and Eric Burgett[1]

This LDRD explores Transient Reactor Test (TREAT) Facility configurations that can facilitate high-resolution, in situ measurements on small nuclear material samples, and the feasibility of mating current microstructure measurement technologies and techniques to the new experimental environment. The in situ microstructure measurements can be performed without impacting the TREAT Facility restart or the nominal mission of the TREAT program and can effectively extend the TREAT mission to include beginning-of-life microstructure separate effects measurements.

During the first year of this project, the focus was on establishing a baseline configuration for utilizing the TREAT Facility for science-based microstructure studies in a way that would not impact the core mission of transient fuel testing for qualification. This effort provided a proof-of-concept design for delivering advanced-science-based separate effects data on fuel performance and underlying phenomena.

A neutronics modeling and simulation analysis was performed to determine the feasibility and baseline requirements for in situ irradiations that could provide high-fidelity imaging and microstructure characterization of fuel samples within the modified TREAT Facility configuration. The analysis produced a design of an irradiation capability utilizing the unused east thermal column of the TREAT Facility for performing separate effects and microstructure studies. In this way, both the macroscopic and the microstructure behavior of the fuel can be studied simultaneously under the same power profile and can take full advantage of the significant "off-cycle" time between transients when the TREAT Facility is in a low-power steady state. The unique pulse structure of the TREAT Facility allows high-resolution imaging in between moderate power pulses, such that the microstructure evolution of fuel materials can be studied as a step-cycle process.

The second and third years of the project focused on the data-handling and imaging algorithms needed to collect in situ data on large samples. Unique to this approach is the potential for simultaneous acquisition of microstructure evolution data from hundreds of features within a single fuel material sample. The challenge comes in automating the identification of salient features and handling the sheer amount of data from acquiring imaging at multiple high resolutions that can be cross correlated with simulation results.

Summary

The TREAT reactor was modeled in an unmodified configuration to compare the impact of the proposed irradiation cavity on the base operations of the TREAT reactor. Four group cross-section neutron contour maps were produced for both the main reactor core, as well as the science-based irradiation system integrated into the TREAT east thermal column.

Both low-enriched uranium and highly enriched uranium irradiation cavities were investigated to optimize the utility of the microstructure characterization capability while minimizing the impact to nominal TREAT reactor transient testing. It was determined that the previously unused thermal column on the east side of the reactor vessel offered sufficient neutron flux and access for sample movement and imaging equipment to develop a parasitic microstructure characterization component to TREAT Facility operations. There is adequate space for a specially designed imaging capability, such as a scanning electron microscope or a backscatter laser in this location. With a system designed for low-enriched uranium, an integrated fast neutron flux of E12 n/cm^2/s is achievable while operating the TREAT Facility in the 100-kW steady-state mode. This would allow for collection of microstructure data continually whenever the TREAT Facility is not being used for transient testing.

[1] Idaho State University

A similar neutronics analysis was performed for a highly enriched, uranium-boosted irradiation cavity in the thermal column in order to achieve an E13 n/cm^2/s integrated flux in the microstructure cavity while operating the TREAT Facility in the 100-kW steady-state mode. Full TREAT core flux profiles were produced for a number of different irradiation scenarios that could be used to characterize microstructures. In addition, a safety envelope was produced to ensure that normal transient testing would not be limited by the inclusion of the irradiation cavity in the east thermal column. It was determined that the irradiation cavity can operate indefinitely in the steady-state mode, and cooling was designed to ensure that the hottest fuel element can survive a 0.5-second 16-GW$_{th}$ pulse in the transient operation. Using an adiabatic boundary with conduction to the coolant flow only, a computational fluid dynamics code that is part of the Fluent and Solidworks package was used to model the hottest fuel element, showing a 53°C temperature rise in the hottest spot.

An additional data-acquisition scenario was investigated to take advantage of the unique pulse structure available at the TREAT Facility. The highly enriched uranium cavity provides 1×10^{15} n/cm^2/s when the TREAT Facility is operated at less than 10 MW, which it can do for a maximum of approximately 200 seconds with a 1-hour cooling time in between pulses. The equivalent fast reactor dose can be delivered in less than five days with high-resolution images collected at the end of each pulse.

Preliminary measurements have been performed to determine the feasibility of scanning electron microscope imaging within the proposed irradiation cavity for the east thermal column. Samples of Cf-252 were fabricated to have fission rates comparable to fresh U-235 samples under irradiation at the proposed steady-state and 10-MW pulse scenarios. High-resolution imaging was achievable for the highly radioactive samples, and these were used to develop a variable magnification imaging algorithm.

Benefits to DOE

Development of these capabilities will make INL a leader in the science-based characterization of the time evolution of microstructural fuel behavior during irradiation. Successful completion of the project would position the TREAT Facility as the premier test site for both beginning-of-life microstructure fuels testing as well as end-of-life transient testing.

The work funded by this LDRD is in line with the larger strategy developed by DOE-NE to shift the paradigm of advanced nuclear fuels development to ensure the nation’s energy security for the future. Separate effects and isolated effects testing will inform new first-principle models to develop a predictive performance capability as fuels research moves forward. This project, in particular, leverages the necessary TREAT Facility investments for fuel qualification and takes advantage of the enormous advances in computing methods and resources.

Publications

A journal article is being drafted to detail the TREAT neutronics analysis. A second article will be written to demonstrate the data handling and analysis capable with the TREAT pulse structure.

14-009—Development of an INL Capability for High-Temperature Flow, Heat Transfer, and Thermal Energy Storage with Applications in Advanced Small Modular Reactors, High-Temperature Heat Exchangers, Hybrid Energy Systems, and Dynamic Grid Energy Storage Concepts

James E. O'Brien, Piyush Sabharwall, Su Jong Yoon, and Xiaodong Sun[1]

Advanced reactor systems require R&D, testing, and qualification for critical systems, structures, and components. To meet these requirements, a highly versatile high-temperature test facility is needed. This project was approved to initiate development of such a capability. Key activities include (a) qualification and testing of critical components in a prototypical high-temperature, high-pressure environment, (b) materials development and qualification, (c) manufacturer and supplier evaluation and development, and (d) fundamental thermal-hydraulics research and associated verification and validation.

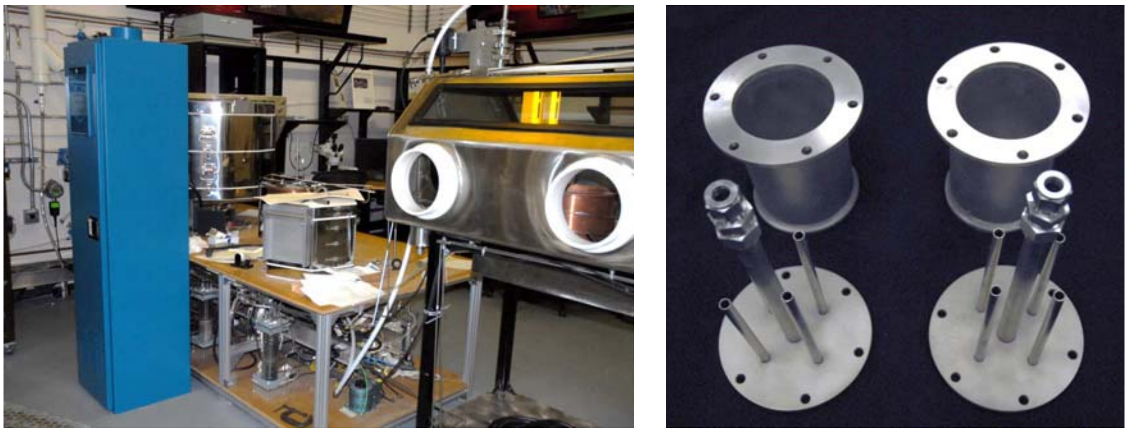
The initial phase of this project (FY 2014) was focused on the development of a conceptual design for a high-temperature, multi-fluid, multi-loop test facility to support heat transfer, flow, materials, and thermal energy storage research for nuclear and nuclear-hybrid applications. In its initial configuration, this facility will include a high-temperature helium loop, a liquid salt loop, and a hot water/steam loop. The three loops will be thermally coupled through an intermediate heat exchanger (IHX) and a secondary heat exchanger. Research topics to be addressed include the characterization and performance evaluation of candidate compact heat exchangers such as printed circuit heat exchangers (PCHEs) at prototypical operating conditions, flow and heat-transfer issues related to core thermal hydraulics in advanced helium- and salt-cooled reactors, and evaluation of corrosion behavior of new cladding materials and accident-tolerant fuels for light water reactors at prototypical conditions. Based on its relevance to advanced reactor systems, the new capability has been named the Advanced Reactor Technology Integral System Test (ARTIST) facility.

Project objectives for FY 2015 focused on technology development and supporting analysis. Computational fluid dynamics (CFD) analyses have been performed for prediction of the flow and heat transfer characteristics of PCHEs. Parameters considered in the analysis include channel hydraulic diameter, header design, channel shape, channel streamwise configuration (zigzag or straight), working fluid, and flow rate. For the zigzag configurations, additional parameters will be considered, including zigzag angle and type of corner (rounded or abrupt). Ohio State University (OSU) is a research partner on this task. OSU has provided experimental data derived from the operation of PCHEs in the OSU high-temperature helium loop, including two straight-channel PCHEs and one zigzag-channel PCHE. Performance data obtained from testing of these heat exchangers will be compared to CFD predictions for code validation. As part of the validation process, a new methodology has been developed for analysis of experimental heat exchanger data, accounting for extraneous heat losses. Significant progress has been achieved with CFD analysis of PCHEs. The latest comparisons to experimental results are very favorable.

In terms of technology development, a laboratory capability for small-scale preparation and purification of fluoride salt mixtures has been developed. This capability will be needed to support the final design and operation of the ARTIST facility at INL. The prepared salt mixtures will be tested for thermodynamic properties such as melting point, heat capacity, and thermal conductivity. The salts will also be used in a pot experiment in which liquid salts will be transferred from one pot to another to validate high-temperature trace heating and flow measurement methods. The working fluid for the initial salt work will be a eutectic mixture of KF-ZrF_4. The salt preparation experience gained through this activity will be directly applicable to the ARTIST facility. Accomplishments related to this activity include the completion of a new laboratory capability for salt preparation, purification, and transfer activities. Purification of fluoride salt mixtures is accomplished by

[1] Ohio State University

hydrofluorination, which removes the moisture/oxide impurities and other contaminants such as chlorine and sulfur. Hydrofluorination is accomplished by HF/H_2/helium sparging of the molten-salt mixture at a temperature of ~450°C. A glovebox has been outfitted to support these salt-related activities. In addition, the laboratory gas-monitoring system has been upgraded to detect HF, and a ventilated gas safety cabinet has been installed to safely house the HF gas. New salt preparation and transfer vessels have been fabricated from Alloy 201 (nickel). Photographs of the laboratory and nickel salt preparation and transfer vessels are provided in Figure 1.



(a) *(b)*

Figure 1. Fluoride salt preparation and purification laboratory (a) and nickle molten salt preparation and transfer vessels (b).

Summary

A detailed conceptual design of a high-temperature, multi-fluid, multi-loop test facility to support heat transfer, flow, materials, and thermal energy storage research for nuclear and nuclear-hybrid applications has been completed. The facility includes three flow loops: a high-temperature helium loop, a liquid salt loop, and a hot water/steam loop. The three loops will be thermally coupled through an IHX and a secondary heat exchanger, both based on the PCHE design. CFD simulations have been performed for prediction of the flow and heat transfer characteristics of PCHEs. CFD results have been validated against experimental data provided by OSU. The experimental PCHE heat transfer results were analyzed using a new methodology that accounts for extraneous heat losses. A new laboratory capability has been developed for small-scale preparation and purification of fluoride salt mixtures. The prepared salt mixtures will be tested for thermodynamic properties such as melting point and heat capacity. The salts will also be used in a pot experiment in which liquid salts will be transferred from one pot to another to validate high-temperature trace heating and flow measurement methods. This project has supported two graduate students at OSU and an INL postdoc.

Benefits to DOE

The DOE Advanced Reactor Technology program supports research, development, and deployment activities designed to promote safety, technical, economic, and environmental advancements of innovative Generation IV nuclear energy technologies. The ARTIST facility will provide a physical test platform for performance and integrity evaluation of relevant components to the Advanced Reactor Technology program at prototypical conditions. Through the use of the ARTIST facility, the technology readiness level of important components such as the IHX can be significantly advanced. The facility will also support fundamental research in three high-temperature test sections for a variety of test, validation, and verification objectives. Supporting technical activities in computational analysis and molten salt technology development aid in the final design and operation of the ARTIST facility at INL.

Publications

O'Brien, J. E., P. Sabharwall, S. Yoon, and G. K. Housley, "Strategic Need for a Multi-Purpose Thermal Hydraulic Loop for Support of Advanced Reactor Technologies," INL/EXT-14-33300, October 2014.

O'Brien, J. E., P. Sabharwall, and S. Yoon, "A Multi-Purpose Thermal Hydraulic Test Facility for Support of Advanced Reactor Technologies," *ANS 2014 Winter Meeting and Nuclear Technology Expo*, Anaheim, California, November 9–13, 2014.

O'Brien, J. E., P. Sabharwall, and S. Yoon, "Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," *ASME International Congress and Exposition, Paper #IMECE2014-39057*, Montreal, Canada, November 14–20, 2014.

Sabharwall, P., J. E. O'Brien, and S. Yoon, "Experimental Facility for Development of High-Temperature Reactor Technology: Instrumentation Needs and Challenges," *International Congress on Advances in Nuclear Power Plants, ICAPP*, Nice, France, May 3–6, 2015.

Yoon, S., K. Wegman, J. E. O'Brien, P. Sabharwall, and Xiaodong Sun, "An Analytical Methodology to Evaluate Thermal-Hydraulic Performance of Compact Heat Exchangers, Accounting for Heat Loss," *2016 International Congress on Advances in Nuclear Power Plants (ICAPP2016), Paper No. 15814*, San Francisco, California, April 17–20, 2016, accepted.

Presentations

"Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," INL Annual Program Review, DOE Germantown Office, September 22, 2015.

"Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," Presentation to Terrestrial Energy, INL, July 15, 2015.

Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," Presentation to Transatomic Power, INL, June 1, 2015.

"Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," Nuclear Science and Technology Peer Review, INL, May 20, 2015.

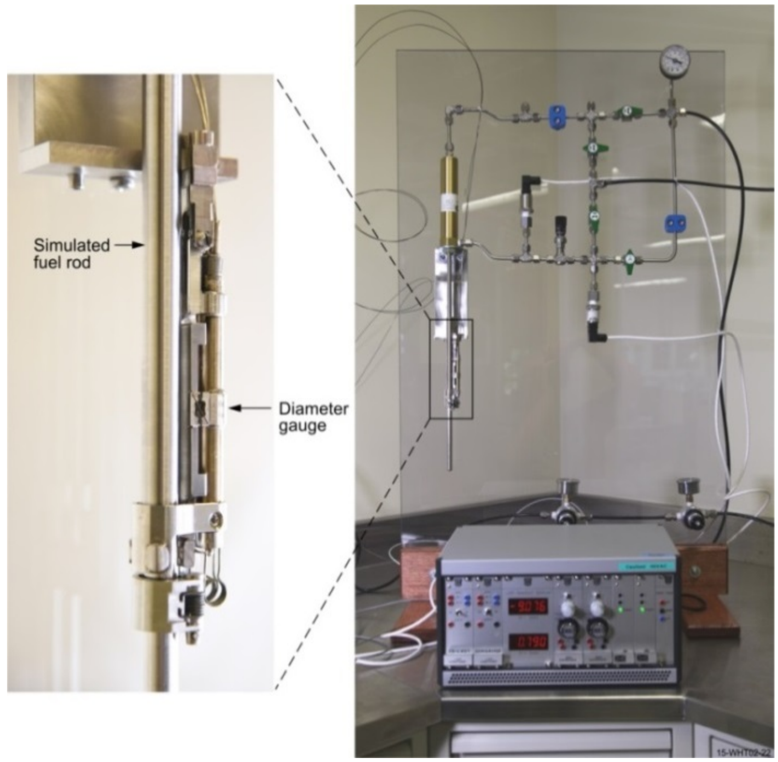
"Development of a Multi-Loop Flow and Heat Transfer Facility for Advanced Nuclear Reactor Thermal Hydraulic and Hybrid Energy System Studies," LDRD Annual Review, INL, May 12, 2015.

"Nuclear Energy in the Context of Today's Energy Challenges," Nuclear Engineering Seminar Series, Ohio State University and University of Cincinnati (video link), Columbus, Ohio, March 26, 2014.

14-010—Use of Linear Variable Differential Transformer (LVDT)-Based Methods to Detect Real-Time Geometry Changes during Irradiation Testing

Darrell Knudson, Kurt Davis, Keith Condie, John Crepeau,[1] and Steinar Solstad[2]

New materials are being considered for fuel, cladding, and structures in advanced and existing nuclear reactors. These materials can undergo significant dimensional and physical changes during irradiation. However, in the United States, the only method currently available for detecting such changes is by repeatedly irradiating a sample for a specified period of time and then removing it from the reactor for evaluation. The time and labor needed to remove, examine, and return irradiated samples for each measurement makes this approach very expensive. In addition, such techniques provide limited data, and handling may disturb the phenomena of interest. These problems are compounded by the fact that capabilities to conduct this type of measurement are not widely available.



(a) (b)

Figure 1. Diameter gauge with simulated fuel rod installed (a) and benchtop testing using constant velocity hydraulic control system (b).

For these reasons, in-pile detection of changes in geometry is greatly needed to understand real-time behavior during irradiation testing of fuels and materials in high-flux U.S. material and test reactors. This project will enable the ATR to deploy advanced linear variable differential transformer-based test rigs capable of detecting in-core, real-time changes in the length and diameter of fuel rods or material samples. In particular, this new INL capability will enable detection of changes in diameter due to crud deposition or pellet-clad interactions during fuel irradiation testing in addition to changes in elongation due to creep. A new advanced test rig will be designed and evaluated that combines an enhanced linear variable differential transformer jointly developed at INL's High-Temperature Test Laboratory (HTTL) and the Institute for Energy at the Halden Reactor Project, a diameter gauge developed by the Institute for Energy, and a controlled-load elongation rig inspired by the Technical Research Center of Finland. Insights and results from test rig evaluations completed by INL and University of Idaho researchers using existing HTTL autoclaves will be used to develop a final test rig design for use in the ATR. This new capability will provide vital support for DOE programs such as the ATR National Scientific User Facility, Fuel Cycle Research and Development, Nuclear Energy Enabling Technology, and Next Generation Nuclear Plant.

[1] University of Idaho

[2] Halden Reactor Project

Summary

The first year of this project was devoted to designing, procuring, fabricating, and initiating benchtop testing to evaluate the performance of a diameter gauge test rig. This year, benchtop testing was completed that not only evaluated the diameter gauge but also provided proof-of-principle for a unique axial measurement approach using constant axial velocity to measure axial displacement (see Figure 1). This approach eliminates the need for additional instrumentation in the active region of the core. A simulated fuel rod was also used to evaluate instrument accuracy and to determine optimal scan rate (axial velocity). The optimal scan rate was determined to be 2 mm/s, and measurement accuracies of ± 3 µm and ± 300 µm were found for the diameter and axial measurements, respectively. During the final year, testing will be moved from the benchtop to the autoclave (Figure 2). These evaluations are essential for ensuring that the diameter gauge will perform with the required accuracy and reliability prior to deployment in an ATR pressurized-water reactor loop.

This research is funding an INL employee completing a University of Idaho graduate degree. In addition, this research helps grow the in-pile instrumentation capability established at INL's HTTL.

Figure 2. HTTL autoclave with controls for heating water and sampling water chemistry in which the diameter gauge test rig will be evaluated.

Benefits to DOE

Development of advanced in-core instrumentation is critical to DOE's energy security mission to provide world-class facilities for advancing nuclear science and technology. Successful completion of this effort will result in a proven test rig that can be used by DOE researchers and industry organizations to obtain real-time data for dimensional changes in fuel and material specimens during irradiation testing in U.S. high-flux materials testing reactors, such as ATR and the Transient Test Reactor facility when it is restarted.

Publications

Davis, K., D. Knudson, J. Rempe, J. Crepeau, and S. Solstad, "Design and Laboratory Evaluation of Future Elongation and Diameter Measurements at the Advanced Test Reactor," *Nuclear Technology,* Vol. 191, pp. 92–105, July 2015.

Presentations

Davis, K., D. Knudson, K. Condie, and J. Rempe, "Measurement of Diameter Changes during Irradiation Testing," 9th International Conference on Nuclear Plant Instrumentation, Control & Human–Machine Interface Technologies (NPIC & HMIT 2015), Charlotte, North Carolina, February 21–26, 2015.

14-025—Minor Actinide and Lanthanide Separations in Alternative Media

Mitchell Greenhalgh and R. Scott Herbst

Since its inception, the nuclear industry, specifically the reprocessing of irradiated nuclear fuels, has realized that the separation of minor actinides (MAs) (e.g., americium and curium) from lanthanides (LNs) and their subsequent recycle into new reactor fuel would greatly reduce the waste generated by reprocessing. However, the separation of MA from LN represents one the most daunting challenges faced by modern-day separation scientists, rivaled in complexity only by isotopic separations. The LN/MA separation is difficult due to the remarkably similar chemical behavior between the LN series (which includes the elements of lanthanum through lutetium, and commonly yttrium) and the MA. The ultimate goal of this project is to develop and test efficient solvent-extraction (SX) flowsheets and equipment for the separation of MA from LN elements in alternative media (i.e., chloride, sulfate, phosphate, or thiocyanate). Traditional nuclear processing separations have focused on nitrate media (HNO_3), and the process equipment (notably constructed from stainless steel) is compatible only with the nitrate media. Industrially, the separation and purification of the LN species typically utilizes chloride media (HCl) and different extractants and diluents than those indigenous to the nuclear industry. Ironically, most of these industrially proven systems have not been evaluated for MA/LN separation despite the inordinately similar chemistry of these elements in solution. Laboratory experiments will be performed to establish the fundamental separations behavior of MA and LN in alternative systems. Experimentally acquired data will be used to develop and test process flowsheets for the most promising separation schemes. Additionally, chemically compatible SX equipment suitable for use in a glovebox or hot cell will be designed, procured, and tested for the new flowsheets with actual radionuclides of interest in laboratory hoods at tracer levels.

Summary

Laboratory experiments to determine the fundamental separation characteristics and behaviors of MA and LN utilizing alternative extractants and nontraditional aqueous media were continued during the second year of this project. Although a separation factor of 50 was obtained for europium/americium in the previous year with the Ionquest 801/chloride system, separation factors of the light lanthanides (i.e., cerium) from americium were quite low. Laboratory experiments will be expanded in the coming year to investigate additional aqueous phases (i.e., sulfate and phosphate), and the feasibility of a metal recycle in the scrub section will be investigated to facilitate this separation. Metal recycle in the scrub section is a technique commonly employed in the rare earth industry to enhance separations. The data obtained from these evaluations will be utilized to develop a full flowsheet for demonstration in chemically compatible SX equipment.

In addition to the laboratory separations testing, 32 stages of small, laboratory-scale, mixer-settler equipment constructed of a Kynar® polymer have been received from Metallextraktion AB of Sweden. This equipment is chemically compatible with all of the proposed alternative media in the project and is also the most radiation-resistant plastic available. The mixer-settler equipment has a maximum throughput of 166 mL/min and a total solution hold up of only 600 mL per stage. The equipment can be operated in a variety of process configurations, which will ultimately be defined by the concurrent laboratory evaluations. The entire 32-stage system only requires approximately 12 linear ft of bench space, making it ideal for testing in a space-limited radiological environment. Initial hydraulic evaluations of the mixer-settler equipment have been performed to define the operating parameters that would achieve the desired separations (i.e., maximum flow rates, mixing speeds, and mass transfer efficiencies). Additional extraction, scrubbing, and stripping tests were performed in multiple stages of the mixer-settlers using the Ionquest 801/chloride system. These tests were performed to evaluate the performance of the equipment for the various sections of the flow sheet and to gain operational experience with the equipment. The results of this testing demonstrated that the equipment will perform as desired for the flowsheet tests anticipated in the coming year.

Benefits to DOE

The chemistry and engineering expertise developed and separations processes being examined are directly relevant to DOE's nuclear fuel cycle mission—in particular, the development of separation capabilities that can be applied to processes different from the norm. The equipment and engineering developments related to process flowsheets are also directly relevant to future nuclear fuel cycle separations. Furthermore, the unique separations capabilities and equipment obtained in this project represent the only location in the United States where such work can be performed. The technical products (journal articles and patents) generated during this project will benefit the advanced separations reputation of INL and DOE. Pending successful outcomes from this project, funding and new programs will be sought from a wide range of DOE and Department of Defense offices with interests in nuclear fuel cycle or other similar separations.

Presentations

Lyon, K. L., M. R. Greenhalgh, and R. S. Herbst, "Minor Actinide and Lanthanide Separations in Alternative Media," 39th Annual Actinide Separations Conference, Salt Lake City, Utah, May 18-21, 2015.

14-026—Multiscale Modeling on Delayed Hydride Cracking in Zirconium: Hydrogen Transport and Hydride Nucleation

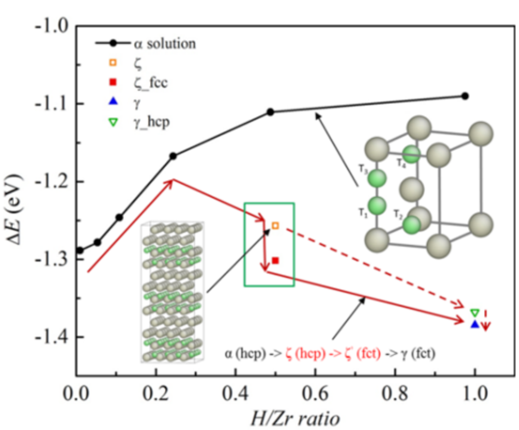
Yongfeng Zhang and Xianming Bai

Formation of hydrides in zirconium-based cladding leads to embrittlement and has been identified as a critical material-science issue affecting the integrity of fuel pins in light-water reactors during storage. While hydrides have been widely characterized by experiments, the transport of hydrogen and the mechanisms for hydride formation have not been fully understood. Using atomistic-scale modeling tools, the objectives of this project are to (a) investigate hydrogen diffusion and segregation and (b) explore the mechanisms for hydride nucleation in α-Zr. The research results and data collected from the atomistic scale will be useful for upper-scale modeling on hydride formation and reorientation that may occur during used fuel disposition.

Summary

This LDRD is in its second year. In FY 2015, the project team focused on homogeneous hydride nucleation in α-Zr and the effect of stress on hydrogen transport. A metropolis Monte Carlo model has also been developed for hydrogen precipitation and hydride formation. In FY 2016, the nucleation of various hydride phases will be studied using coupled molecular dynamics (MD) and metropolis Monte Carlo simulations. A material model describing the effect of stress/strain on hydrogen diffusion in zirconium will be implemented into the MARMOT code to improve upper-scale models for hydrogen diffusion and hydride formation.

Using the charge-optimized many-body potential, a nucleation path for homogeneous hydride formation in α-Zr has been revealed by MD simulations. Hydrogen has limited solubility in α-Zr. Once the solubility limit is exceeded, the stability of solid solution gives way to that of coherent hydride phases, such as the ζ-hydride by planar precipitation of hydrogen atoms, as shown in Figure 1. At finite temperatures, the ζ-hydride goes through a hexagonal close-packed/face-centered cubic transformation, forming a mixture of γ-hydride and α-Zr, which can further grow into a γ-hydride cluster. It is further found that the hexagonal close-packed/face-centered cubic transformation is thermodynamically favored with a negligible barrier. The mechanism observed here is consistent with literature results and is believed to be relevant at reactor operating temperatures. The charge-optimized many-body potential has been found useful for hydride nucleation during this work, with several deficiencies identified on other important properties, including hydrogen transport. For better atomic-scale understanding of hydrogen behavior in zirconium, a subcontract has been signed with the University of Florida to improve this potential for hydrogen diffusion and planar defects in zirconium matrix.



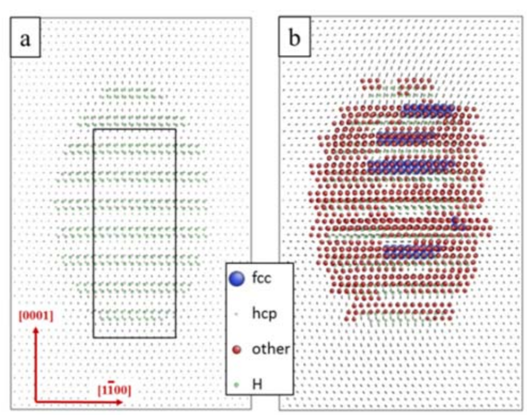
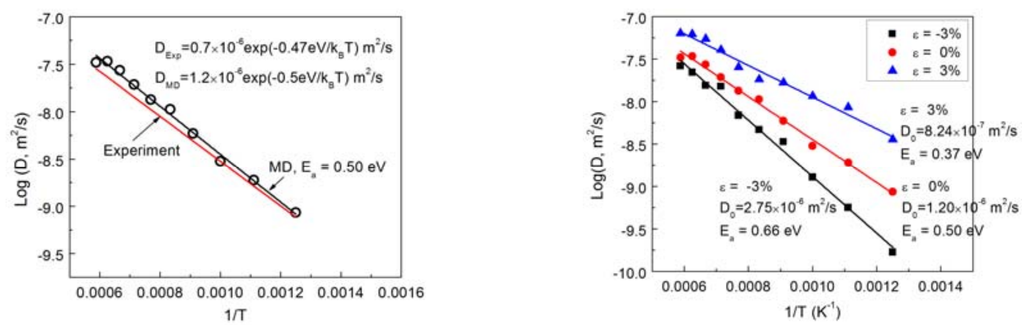


Figure 1. Hydrogen solution energy as a function of the hydrogen/zirconium ratio (left) and atomic configurations showing the structural transformation of an embedded ζ-phase cluster to a γ-hydride nucleus at 600 K (right).

In addition to hydride nucleation, the diffusion of hydrogen in α-Zr has also been studied using the reactive force-field potential for the purpose of elucidating the effect of stress. In MD simulations, the diffusivity of hydrogen can be calculated by computing the mean square displacement at a given temperature. The prefactor and activation barrier of the diffusivity can be obtained by plotting the logarithmic hydrogen diffusivity as a function of inverse temperature. As shown in Figure 2(a), the diffusivity given by independent MD simulations from this LDRD agrees well with previous experimental measurement in literature. Furthermore, it is found that the diffusivity of hydrogen can be significantly affected by the stress state. As shown in Figure 2(b), tensile stress/strain enhances hydrogen diffusion by reducing the barrier, and compressive stress does the opposite. This effect is important for hydrogen transport and hydride formation at stress risers such as crack tips.



(a) *(b)*

Figure 2. Logarithmic H diffusivity as a function of inverse temperature from MD and experiments (a) and under various stress states (b). Tensile stress is positive, and compressive stress is negative.

Benefits to DOE

The outcome of this project largely advanced the researchers' understanding of hydride formation, including the nucleation mechanism of hydride and the effect of stress on hydrogen transport. Furthermore, some of the data generated from this project can be used in upper-scale modeling. The knowledge derived from this project aids in evaluating the detrimental effect of hydrides on used fuel during extended storage periods and thus the risk in nuclear waste management with relevance to the mission of nuclear safety and energy security.

Publications

Zhang, Y., X. Bai, J. Yu, M. R. Tonks, M. Noordhoek, and S. Phillpot, "Homogeneous hydride nucleation pathway in Zr: molecular dynamics simulations with the charge-optimized many-body potential," under review.

Presentations

Zhang, Y., W. Xu, P. Millett, and Y. Zhu, "Inter-facet Vacancy Diffusion and Void Nucleation in Hcp Metal," MRS 2014 Fall Meeting, Boston, Massachusetts, November 30–December 5, 2014.

Zhang, Y., X. Bai, M. Noordhoek, and S. Phillpot, "Molecular Dynamics Simulations of Zr/Zr-hydride Interface with the Charge Optimized Many Body (COMB) Potential," TMS 2015 Meeting, Orlando, Florida, March 15–19, 2015.

Zhang, Y., X. Bai, J. Yu, M. R. Tonks, M. Noordhoek, and S. Phillpot, "Molecular dynamics simulations on homogeneous hydride nucleation in alpha-Zr," TMS 2015 Meeting, Nashville, Tennessee, February 14-18, 2016, accepted.

Bai, X., Y. Zhang, and M. R. Tonks, "Computer Modeling of Hydrogen and Oxygen Transport during Zirconium Corrosion," TMS 2016 Meeting, Nashville, Tennessee, February 14–18, 2016, accepted.

14-031—Multidimensional Multiphysics Modeling of Fuel Behavior during Accident Conditions

Richard Williamson, Jason Hales, Giovanni Pastore, and Stephen Novascone

Developing computational tools for reliably predicting the thermo-mechanical behavior and lifetime of nuclear fuel rods during abnormal reactor events is essential from both a safety and an economic standpoint. Fuel performance codes able to accommodate accident analysis are needed for safety analysis and design purposes, as well as for the development of accident-tolerant fuel concepts, which has become priority at DOE since the 2011 Fukushima Daiichi Nuclear Power Plant accident. The current research aims to develop an advanced tool for the improved analysis of accident fuel behavior relative to traditional modeling, leveraging the unique capabilities of INL's fuel performance code known as BISON. The focus is on the UO_2 fuel—Zircaloy cladding rods employed in current light-water reactors and on simulation of loss-of-coolant accidents (LOCAs), which is topical following the Fukushima accident.

Summary

Several limitations exist in current fuel performance codes, including simplistic 1.5-dimensional approximation, loosely coupled physics, and the need for separate codes for normal operation and accident analysis. This project currently focuses on achieving significant advances relative to state-of-the-art analysis of nuclear fuel involved in accidents, building on INL's multidimensional, multiphysics, fully coupled fuel performance code BISON. To capture the additional physics and increased complexity due to accident conditions relative to normal reactor operation, new models are developed and incorporated in the code. This requires consistently accounting for mutual interactions among such models as interdependent phenomena that are represented, as well as ensuring consistent matching with the global framework of BISON. Such code expansion results in the capability to represent the peculiar phenomena occurring during accidents and to consistently enclose such additional physics in a global fuel rod analysis. The outcome is a tool that is able to model integral fuel rod behavior during both normal reactor operation and accident conditions beyond the limitations of traditional analysis and with improved accuracy.

During the first two years of the project, models for all main phenomena involved in light-water reactor fuel rod behavior during LOCA conditions were developed, consistently incorporated in BISON, and validated. In particular, key accomplishments to date include models for (a) transient fission-gas release coupled with gaseous swelling, (b) rapid steam-cladding oxidation, (c) Zircaloy solid-solid phase transformation, (d) hydrogen generation and diffusion in Zircaloy, (e) Zircaloy high-temperature nonlinear mechanical behavior (high-temperature creep), and (f) burst failure of Zircaloy cladding. Figure 1 (a and b) illustrates some results relative to application of BISON with these new, mutually coupled models to a first-time, three-dimensional simulation of a cladding ballooning-burst test representing LOCA conditions. A visual inspection image of a burst-failed fuel rod is also reported [Figure 1(c)]. Moreover, validation of the extended code through quantitative comparison of results against an extensive data set from ballooning-burst experiments was performed. As an example, comparisons between calculated and measured fuel rod inner pressure at the time of burst are shown in Figure 1(d), demonstrating a satisfactory accuracy of BISON predictions. Ultimately, application of the code to modeling global fuel rod behavior during LOCAs is now possible, so that validation against integral experiments has begun. Figure 2 refers to a preliminary simulation of the IFA-650.2 Halden LOCA test. The code consistently reproduces the trend of rod inner pressure during ballooning and predicts the time to failure with encouraging accuracy.

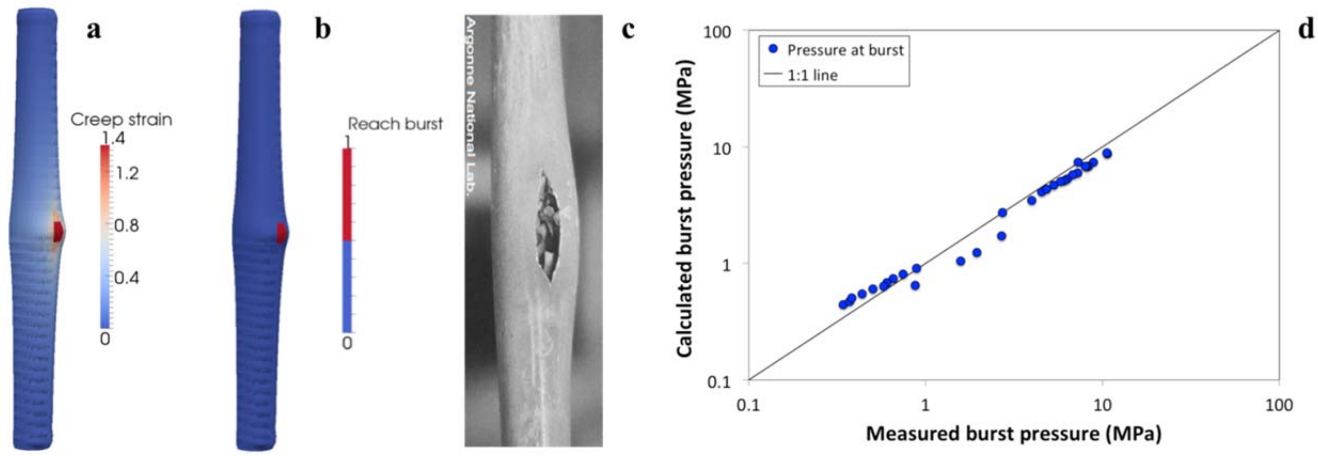


Figure 1. Contour plots for a BISON three-dimensional simulation of a cladding ballooning-burst test, including creep strain magnitude at (a) time of burst and (b) burst failure zone. Visual inspection of a burst-failed fuel rod following a LOCA is shown in (c). Comparison of BISON results and experimental data for 31 simulated experiments is shown in (d).

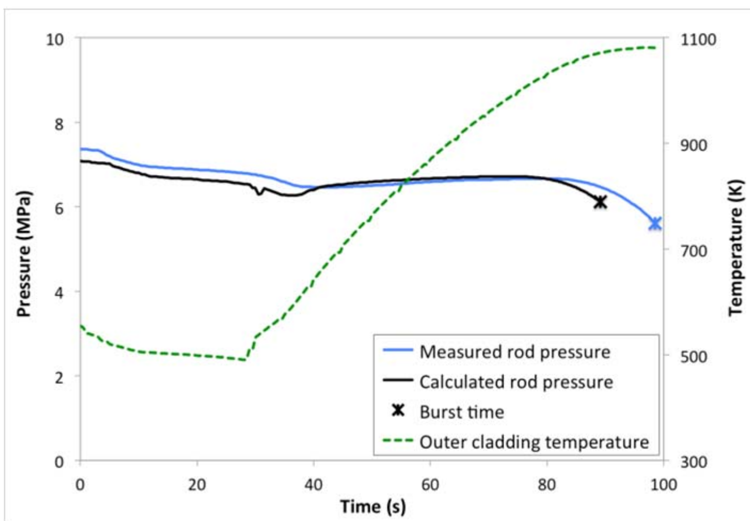


Figure 2. BISON results and experimental data for the IFA-650.2 Halden integral LOCA test.

The project work has been presented at three international meetings. In the framework of this LDRD, DOE participates in the Coordinated Research Project on Fuel Modeling under Accident Conditions, which is sponsored by the International Atomic Energy Agency. Moreover, important international collaborations relevant to the LDRD have been established with the European Commission's Institute for Transuranium Elements (Germany), Politecnico di Milano University (Italy), and Organization for Economic Cooperation and Development (OECD) Halden Reactor Project (Norway). An assignment at the Halden Reactor Project for an INL employee on BISON modeling of Halden LOCA tests is under way. Also, a joint Ph.D. project among INL, the Institute for Transuranium Elements, and the Politecnico di Milano University has been set up, with a student internship at INL. Further collaborative work and internships are planned for FY 2016.

Benefits to DOE

The current LDRD directly benefits the nuclear energy mission of DOE by addressing one of today's most critical nuclear energy concerns, design basis accidents. Following the Fukushima accident, and given the experimental evidence from programs such as the Halden Reactor Project, understanding LOCAs and reducing their likelihood are key efforts. The work advances the state of the art of fuel modeling, providing the ability to explore accident behavior in a novel and improved way, with fully coupled solutions to multidimensional problems. The LDRD represents a strong addition to the current nuclear fuel modeling efforts at INL and further demonstrates INL's developing excellence in modeling and simulation science. Finally, the project benefits DOE's goal of developing enhanced accident-tolerant fuels.

Publications

Chakraborty, P., M. R. Tonks, and G. Pastore, "Modeling the influence of bubble pressure on grain boundary separation and fission gas release," *Journal of Nuclear Materials*, Vol. 452, pp. 95–101, 2014.

Pastore, G., S. R. Novascone, R. L. Williamson, J. D. Hales, B. W. Spencer, and D. S. Stafford, "Modeling of Fuel Behavior during Loss-of-Coolant Accidents using the BISON Code," *Proceedings of the Reactor Fuel Performance Meeting – Top Fuel 2015*, Zurich, Switzerland, September 13–17, 2015.

Pastore, G., D. Pizzocri, J. D. Hales, S. R. Novascone, D. M. Perez, B. W. Spencer, R. L. Williamson, P. Van Uffelen, and L. Luzzi, "Modelling of Transient Fission Gas Behaviour in Oxide Fuel and Application to the BISON Code," *Proceedings of the Enlarged Halden Programme Group Meeting*, Røros, Norway, September 7–12, 2014.

Presentations

Pastore, G., D. Pizzocri, J. D. Hales, S. R. Novascone, D. M. Perez, B. W. Spencer, R. L. Williamson, P. Van Uffelen, and L. Luzzi, "Modelling of Transient Fission Gas Behaviour in Oxide Fuel and Application to the BISON Code," Enlarged Halden Programme Group Meeting, Røros, Norway, September 7–12, 2014.

Pastore, G., S. R. Novascone, R. L. Williamson, J. D. Hales, B. W. Spencer, and D. S. Stafford, "Modeling of Fuel Behavior during Loss-of-Coolant Accidents Using the BISON Code," Reactor Fuel Performance Meeting – Top Fuel 2015, Zurich, Switzerland, September 13–17, 2015.

Williamson, R. L., G. Pastore, S. R. Novascone, J. D. Hales, B. W. Spencer, and D. M. Perez, "Modeling LOCA behavior with the BISON fuel performance code," 20th QUENCH Workshop, Karlsruhe, Germany, November 11–13, 2014.

14-036—Innovative Research for Fieldable Nuclear Measurements

David L. Chichester, James T. Johnson, Mathew T. Kinlaw, Scott J. Thompson, and Scott M. Watson

This project seeks to evaluate the potential of integrating recent developments in the field of radiation measurement instrumentation with advances in the development of low-power, high-performance, single-board computers to implement transformational advances for in-the-field nuclear measurements for emergency first responders and safeguards inspectors. These advances include new concepts for portable instrumentation for monitoring radiation fields, such as would be needed for securing a nuclear facility, and new approaches to search and respond to nuclear and radiological emergencies. Also of great interest in this area are emerging concepts and enabling technology related to wearable computing.

Summary

Over the next decade, emergency response organizations will create a large demand for a new wave of instrumentation as their first-generation radiation-detection and -measurement systems reach the end of their service lives (10–20 years). New research must begin now in order to have new concepts and approaches ready for the future. One likely area where change will occur in this new wave of instrumentation will be the adaptation and use of networked, distributed sensors. Recognizing this, this project is exploring how the remote telemetry and analysis of geospatial radiation data can be used to improve the detection and assessment of radiological hazards.

In its first year, the project focused on research activities in four areas: (1) exploring methods for using scintillating fiber-optic sensors under field conditions; (2) examining the use of next-generation, internet-protocol-based electronic systems for powering and using gas-filled radiation detectors; (3) examining technology solutions suitable for deploying very lightweight, energy-efficient radiation detectors; and (4) expanding capabilities for programming handheld computer devices, such as smart phones and tablets, to interface with detector instrumentation while simultaneously logging measurement results with phone/tablet metadata, such as Global Positioning System (GPS) coordinates. Topic Area 3 in this scoping study showed the most promise for having impactful results likely to lead to new instruments and methods for radiation measurements in the field.

During its second year, the project focused on the development and demonstration of mobile radiation-monitoring instrumentation coupled with real-time telemetry to transmit gamma-ray dosimetry data, gamma-ray spectral data, neutron dosimetry data, and GPS data. A telemetry module was assembled from commercial off-the-shelf components, including a Raspberry-Pi microcomputer, an onboard GPS receiver, a dual-mode WiFi system, a long-range radio for communications, and customized software with a control-hub interface. This equipment is being used to develop and test new operational concepts for response teams to use when responding to radiological and nuclear emergencies. Figure 1 is a photograph of the telemetry module coupled with a two commercial health-physics survey instruments. The system weighs less than 1 kg and serves as an ideal tool for follow-on research planned for deploying a lightweight, low-power-consumption detector system.

Figure 2 shows examples of raw and post-processed survey data collected with the Fluke 451B coupled with the telemetry box. In the image on the left in Figure 2, each dot represents the average dose rate measured by the Fluke 451B over a one-second period and overlaid on a Google Earth aerial image; the data were collected using the Fluke 451B from the test area for about two hours. A radioactive source was located near the center of the test area. Purple and blue dots represent lower ambient dose fields, and yellow and red represent higher fields. In the image on the right in Figure 2, the data have been smoothed using a modified-Kriging algorithm.

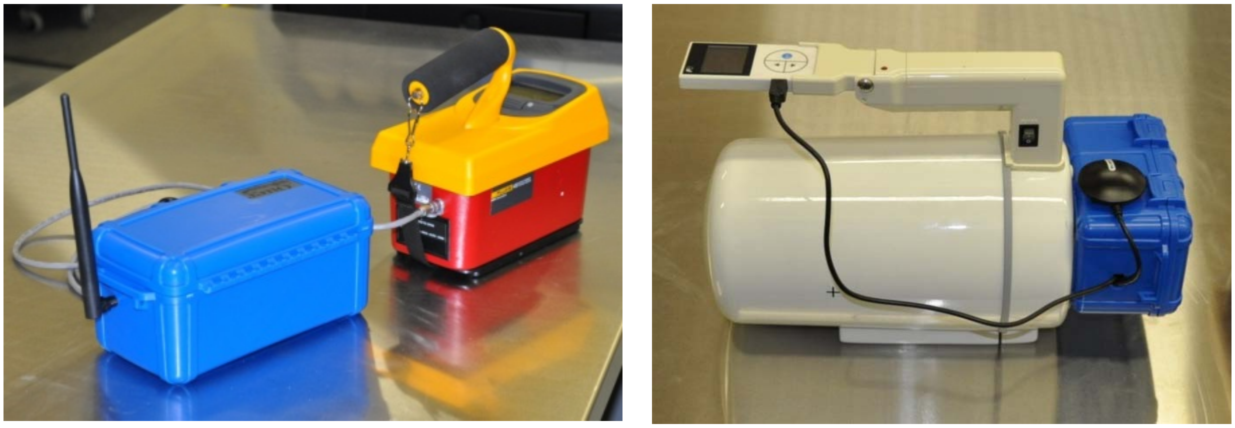


Figure 1. Photographs showing the telemetry system (blue box) connected to two commercial health-physics survey instruments. On the left is the Fluke 451B photon/beta survey instrument; on the right is a Fuji NSN3 neutron survey instrument.

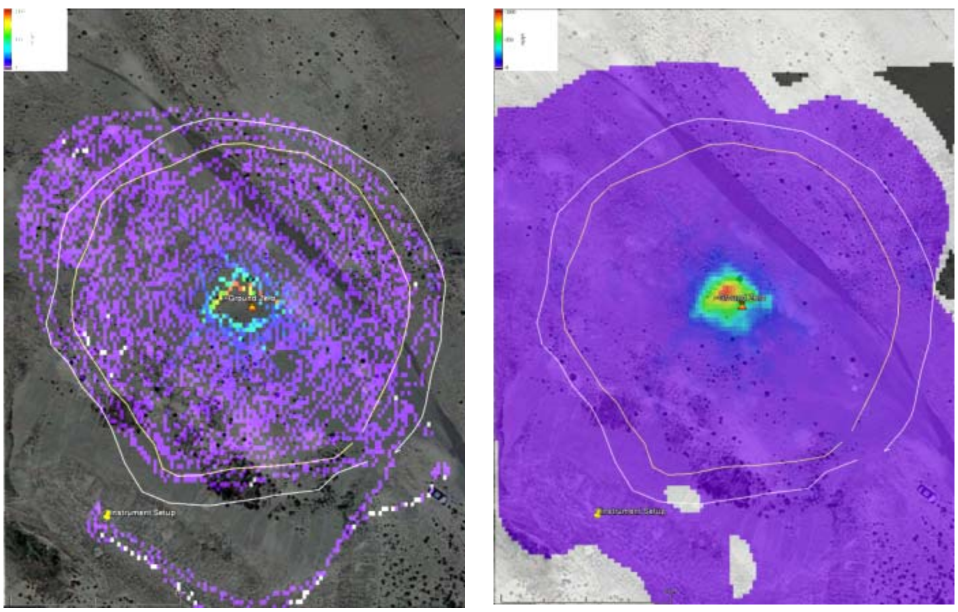


Figure 2. The image on the left shows raw geospatial dose-rate data collected with the Fluke 451B as it was used to survey a large radiological source at INL. The image on the right shows a smoothed, interpolated dose map based on the raw data.

Benefits to DOE

This project benefits DOE by helping to further its leadership role in the science and engineering of advanced nuclear detection technology. This work supports the next generation of nuclear power through the development of new diagnostic tools and capabilities that can be used in radiation monitoring and nuclear safeguards. The technology explored in this project may also have future applications in the areas of used nuclear fuel transportation and storage and may facilitate new concepts for safe and secure interim spent fuel storage.

14-037—Development of Advanced Nuclear Material Characterization Technology for Security Applications

David L. Chichester, James T. Johnson, Mathew T. Kinlaw, Scott J. Thompson, and Scott M. Watson

Emerging nuclear nonproliferation, counterproliferation, and forensic challenges facing the United States require new technological developments in the area of radiation measurement. Often, research programs addressing these areas focus on one type of sensor and one particular observable. The hypothesis of this project is that the integrated use of orthogonal radiation measurement technologies for detecting and analyzing observables will improve the ability to characterize these materials over using these technologies separately. This project is exploring new sensor combinations that can be used in support of national objectives for detecting nuclear and radiological materials.

Summary

Traditional active neutron interrogation (ANI) signatures (such as prompt-neutron die-away analysis, delayed neutron analysis, and delayed gamma-ray analysis) have each been shown to be useful as diagnostic methods for detecting shielded special nuclear material (SNM) or for verifying the absence of SNM within inspected items. However, comparatively less work has taken place to explore the use of these measurement techniques for characterizing assemblies of shielded SNM to determine attributes such as SNM mass, composition, or configuration. In contrast, time-correlated neutron analysis methods such as thermal-neutron coincidence counting and thermal-neutron multiplicity counting are proven measurement techniques for characterizing SNM.

Experiments were performed at INL's Zero Power Physics Reactor to explore the potential for integrating traditional ANI signatures from SNM with time-correlated neutron analysis methods. This work used an array of neutron detector modules specially designed at INL for use in ANI along with a newly acquired list-mode data-acquisition system. This new data-acquisition system is capable of individually recording the relative time of arrival of neutron-detection events in the array in relation to an arbitrary reference time (for passive measurements and for interrogation using steady-state neutron sources) or in relation to synchronization time stamps from a pulsed electronic neutron generator. Measurements were performed using varying configurations of INL's MARVEL test assembly of metallic, highly enriched uranium (HEU). The maximum HEU mass used in these trials was 14.35 kg. The material was used bare, reflected with 5 cm of polyethylene, and reflected with 5 cm of tungsten (W). Neutron multiplication levels ranged from 1.8 (5.49 kg of HEU, bare) to 8.8 (14.35 kg of HEU, reflected with 5 cm of polyethylene). Photographs of two test configurations are shown in Figure 1.

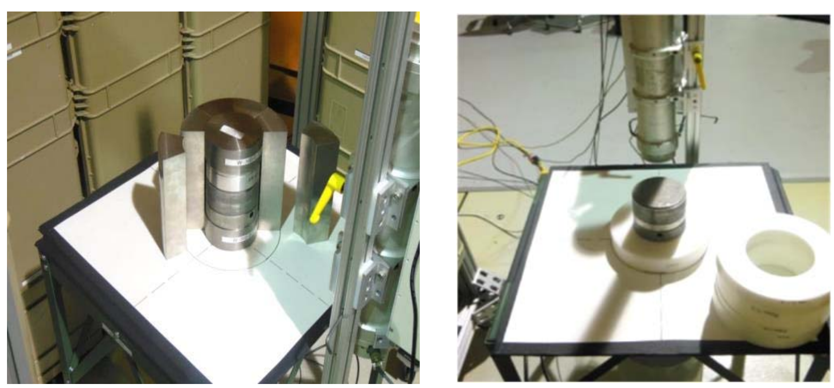


Figure 1. Test setup for interrogating HEU assemblies. The photograph on the left shows two HEU disks in contact with each other within a 5-cm-thick tungsten shell (some parts were removed to see the inside). The photograph on the right shows the same two HEU disks, this time with a 2-cm-thick aluminum disk in between them; 5-cm think polyethylene rings are placed to the side prior to being lowered around the HEU.

Example results from these experiments are shown in Figure 2. These three examples show cases where (a) the HEU mass is the same, (b) the HEU multiplication level (determined empirically and through simulation) is the same, and (c) both the HEU mass and multiplication level are the same. For each case, considering both the die-away and the β-delayed neutron signals, clear differentiation between the different scenarios is possible within a few minutes. In contrast, for these three cases, it is unlikely that either passive gamma-ray spectrometry or passive-gross or time-correlated neutron counting alone could be relied upon to independently detect the scenario differences.

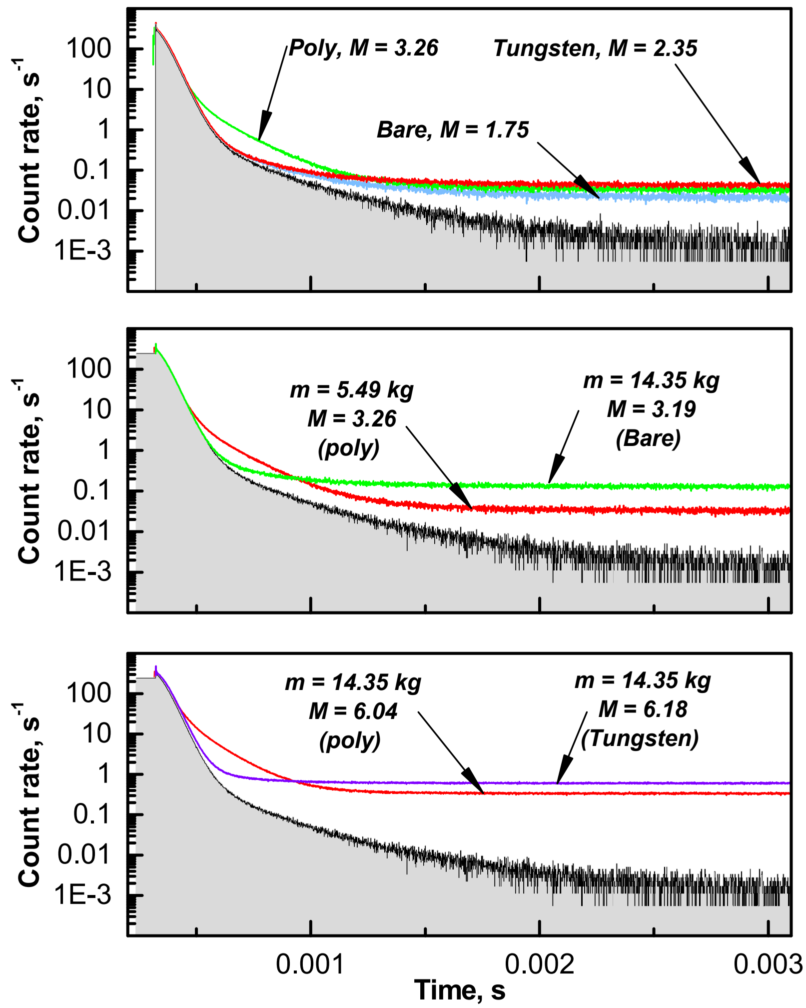


Figure 2. Three figures comparing the inter-pulse neutron signatures observed from differing assemblies of HEU. Top (same mass): three distinct signals for cases where the HEU mass is constant and the reflector multiplication values vary. Middle (same multiplication): two cases where the multiplication is nearly the same but the mass and reflector vary. Bottom (same mass and multiplication): two cases where mass and multiplication are nearly identical but the reflector varies.

Benefits to DOE

This project benefits DOE by advancing the science and engineering principles for the development of advanced diagnostic instruments and methods capable of characterizing shielded assemblies of SNM, in particular HEU. New characterization capabilities that are being developed in this project have relevance across a number of DOE focus areas, including criticality safety, used fuel storage, nuclear facility operations, nuclear nonproliferation, safeguards, arms control, and treaty verification.

Publications

Chichester, D., S. Thompson, M. Kinlaw, J. Johnson, J. Dolan, M. Flaska, and S. Pozzi, "Statistical Estimation of the Performance of a Fast-Neutron Multiplicity System for Nuclear Material Accountancy," *Nuclear Instruments and Methods in Physics Research A*, Vol. 784, pp. 448-454, 2015.

Presentations

Chichester, D., M. Kinlaw, S. Watson, J. Kalter, E. Miller, and W. Noonan, "Experiments and Simulations of the Use of Time-Correlated Thermal Neutron Counting to Determine the Multiplication of an Assembly of Highly Enriched Uranium," Institute of Electrical and Electronics Engineers Nuclear Science Symposium, Seattle, Washington, November 2014.

14-038—Multivariate Calibration of Complex Simulation Codes Using Disparate Types of Evidence: Advanced Automated Validation of Modeling and Simulation Tools

Curtis Smith, Robert Youngblood, Cristian Rabiti, Doug Burns, and Jacopo Buongiorno[1]

Large-scale or complex codes for simulation of facility safety may contain parameters or models that are not known precisely. This limits confidence in the simulation results. To be able to use the results of these simulation codes with confidence, it is important to learn as much as possible about the behavior of these codes. Information from tests (i.e., experiments, both old and new) or operating experience has typically been 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 allow for significant improvements in classical ways of doing both calibration and validation. Recently, key innovations have come from the development of code surrogate approaches (emulators) and Bayesian approaches.

The objective of this LDRD is to develop a validation and quantification approach that will achieve the following:

1. Compare, via a probabilistic method, experimental data with simulation model results using a computerized and automated approach
2. Approach validation from a probabilistic perspective for comparison (as compared to traditional qualitative comparisons)
3. Apply a quantitative method that focuses on those parts of simulation model outputs that are more important (for example, steady state is less important than transient behavior)
4. Use emulators to assist in the model assessment
5. Provide storage of experimental data to automate retrieval for quantification
6. Be automated to determine acceptance of the validation results for a specific simulation model.

Summary

The project team investigated three areas: use of emulators for validation, probabilistic validation approaches, and tools to support validation approaches.

One of the key outcomes of this LDRD is prototyping an approach to quantify the validation case for complex modeling and simulation tools. This work relies on a state-of-the-art probabilistic validation capability to calibrate/assess next-generation software being produced. However, one (potential) way to explore uncertainty for long-running, complex nuclear codes is to use emulators (or reduced-order models). The project team demonstrated how to use emulators to facilitate exploring the "state space" for validation purposes. These emulator-based approaches represent complex phenomena that are very fast running; for example, some of the demonstrations showed a speed-up in computational time on the order of 300–700 times. The focus of the emulators with the LDRD has been on Gaussian process-based models to perform emulator-based Bayesian calibration process.

The second focus of the LDRD was on probabilistic validation. This approach relies on generating probabilistic statements (via probability distributions) for both the code outputs and the data (experiments) to be used for validation. The team explored using distance types of measures where "closeness" between calculated and

[1] Massachusetts Institute of Technology

observed results are given higher scores than cases were the two are not close. These types of measures can be used to provide quantitative results of code validation.

Lastly, the team developed and added data management capabilities to the RAVEN tool in order to facilitate the efficient evaluation of software validation. The focus has been on the creation of capabilities to render “raw” data files (e.g., comma-separated value files) to the internal RAVEN data storage system. Once in RAVEN, probabilistic validation can be performed by using the statistical capabilities of the RAVEN code to compare experimental and simulation data.

Benefits to DOE

DOE-NE’s mission relies increasingly on using large-scale 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 a new simulation capability. This project has led to a state-of-the-art improvement in calibrating these simulations and validating codes so that they better predict reality. The work resulting from this LDRD will be leveraged into future direct-funded projects focusing on validation, for example, for the Light Water Reactor Sustainability Program and the Risk-Informed Safety Margin Characterization Toolkit.

14-041—Uranium Nitride-Uranium Silicide Composite Ceramic Fuel Production via Spark Plasma Sintering

Paul A. Lessing, Robert C. O'Brien, and Jason Harp

The goal of the work performed on this project during FY 2015 was to continue the feasibility assessment of fabricating composites of uranium mononitride (UN) and uranium disilicide (U_3Si_2) using the spark plasma sintering (SPS) process and extend the initial R&D to explore net shape production of prototypical fuel pellets. The specifically desired microstructure was designed to create microencapsulation of UN particles by amorphous U_3Si_2. A volume fraction of 60% UN in a 40% U_3Si_2 matrix was examined to provide a sufficient uranium atom density in the composite such that these compacts may be used as a replacement for UO_2 fuel pellets in existing and future power reactors.

Summary

The SPS process uses rapid pulses of direct current at voltages of up to 10 V and typical current densities of the order 103 A/cm^2 to 104 A/cm^2 to sinter powdered materials held within a conductive die. The sintering mechanisms that take place during SPS are highly dependent on the electrical properties of the materials being processed. For electrically conductive materials, the process promotes initial rapid joule heating at high resistance points across the microstructure. For nonconductive materials, the rapid joule heating of the surrounding die results in rapid heating of the powdered materials enclosed via thermal conduction, which in turn promotes grain boundary diffusion and surface diffusion.

One of the fundamental objectives for FY 2015 was to demonstrate the feasibility of net shape production of composite fuel pellets to prototypical geometries. In order to accomplish this, initial work in FY 2015 was performed to design, fabricate, and develop a new configuration of SPS tooling that would produce final pellet geometries with the highest possible density when completely closed. This tooling has successfully demonstrated repeatable production of prototypical pellets without any requirement for refurbishment or repair. Figure 1 is a photograph of a prototypical pellet produced by this tooling. An invention disclosure for this tooling is being drafted and submitted for patent application review.

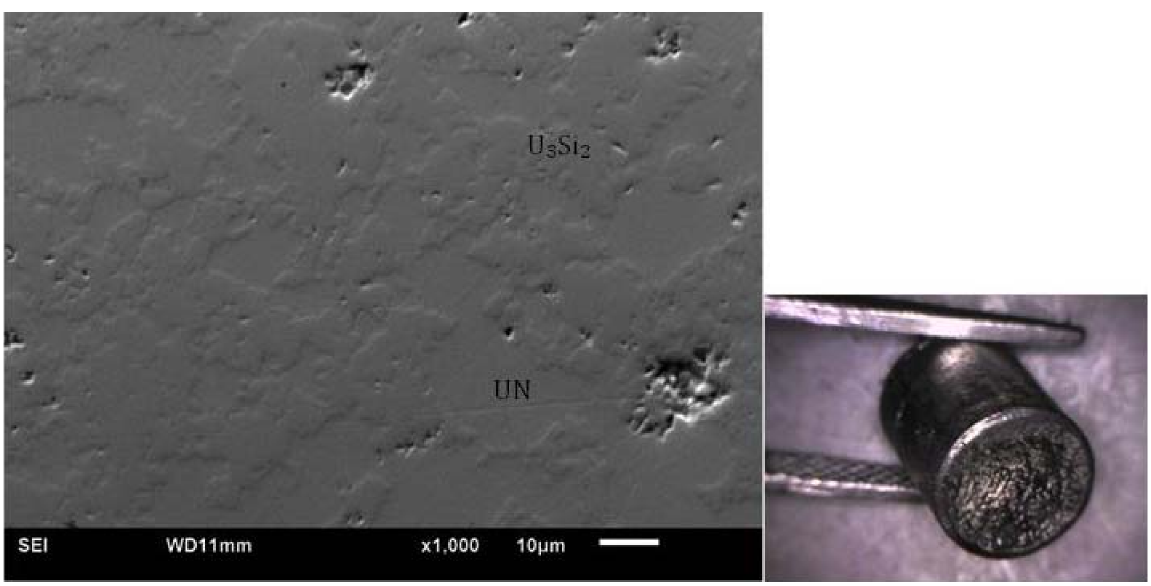


Figure 1. Scanning electron microscope image of a prototypical fuel pellet (left) that was sectioned for microscopy (right). Pullout due to polishing is seen in localized regions of the image.

Preliminary results have successfully demonstrated the feasibility of producing sintered composites of UN-U_3S_{i2} to high density via the SPS process. The work performed in FY 2014 identified that a peak sintering temperature of 1,300°C was required to produce an amorphous U_3Si_2 phase around a dispersion of UN particles. The work in FY 2014 also identified minor challenges with the formation/decomposition of U_3Si_2 to form localized elemental silicon phases during high-temperature sintering. In FY 2015, this challenge was solved through the application of a controlled cooling schedule. Evidence conclusively shows that the UN-U_3Si_2 composite was densified by liquid phase sintering where the U_3Si_2 phase surrounds every grain of UN. This is illustrated in Figure 1, which shows the more corrosion-resistant phase (U_3Si_2) has melted and completely surrounded each of the UN grains. Liquid-phase sintering enhancement requires a molten second phase that wets and spreads on powder surfaces within a compact. Figure 1 shows clear evidence that all four stages of liquid-phase sintering (wetting, rearrangement, dissolution-re-precipitation, and agglomeration) have occurred and that elemental silicon phases can be significantly reduced by means of controlled cooling.

A boiling water corrosion experiment was also set up at INL's Center for Advanced Energy Studies facility involving collaboration with a Boise State University student. The experiment emulated the conditions of reflood of a reactor vessel with portable water over pellets that had been exposed from failed fuel claddings. The corrosion rate and pellet mass trend as a function of exposure time to boiling potable water was measured. Additionally, water chemistry was analyzed using an ion-coupled plasma mass spectrometer as a function of time to determine dissolved uranium concentration. To date, experimentation has been demonstrated using surrogate materials, and approval to proceed with experimentation with U_3Si_2-UN composite pellets has been granted to commence at the start of FY 2016.

Benefits to DOE

Fuel pellets composed of a composite matrix of U_3Si_2 and UN are of interest as an accident-tolerant, high-density uranium dispersion fuel form for light-water reactors. Specifically, these pellets might be a direct substitution for metallic fuels or UO_2 fuels in existing light-water reactors. Also, the improved thermal conductivity of the U_3Si_2-UN fuel increases the safety margin of the reactor.

Publications

O'Brien, R. C., P. A. Lessing, and J. Harp, "Fabrication of UN-U_3Si_2 Composite Fuel Pellets via Spark Plasma Sintering," article in review (2015) for *Journal of Nuclear Materials*.

Presentations

O'Brien, R. C. and P. A. Lessing, "Fabrication of UN-U3Si2 Composites via Spark Plasma Sintering," LDRD Review Meeting, March 13, 2015.

Invention Disclosures

INL invention disclosure record in draft (September 2015).

14-045—End-to-End Radiation Detector Enhancements for Improved Safety and Security in Safeguarded Facilities

Scott J. Thompson, David L. Chichester, Daniel Shy, and Mara M. Grinder

The objective of this project is to demonstrate that radiation-detection systems, such as portal monitors, located at safeguarded facilities can be significantly enhanced through an end-to-end improvement of the scintillation-based detection equipment used within these systems. The use of advanced simulation and modeling techniques in unison with benchmark laboratory testing will allow the project team to optimize the physical layout and light-collection properties associated with the detectors' scintillating crystals for heightened sensitivity to radioactive material. System security can also be enhanced through the application of INL-developed data-protection methods to transmitted data, reducing the risk of monitor spoofing, data corruption, and eavesdropping. These improvements will not only strengthen efforts to safeguard nuclear materials within facilities, but they also have the potential to enhance the radiation safety measures that protect a site's workforce.

Summary

The second year of this project focused on applying spectral deconvolution techniques to unfold the photon fluence incident on a detector from a measured spectrum. These types of numerical techniques provide a way to perform high-resolution spectroscopy while using lower-resolution detection technologies. Several deconvolution algorithms are built into the ROOT Data Analysis Framework developed by the European Organization for Nuclear Research. Each of these algorithms requires a well-defined detector response matrix for unfolding. A lanthanum bromide ($LaBr_3$) scintillator was modeled in MCNP6 in order to calculate this matrix. The matrix ranged from incident energies of 0 to11 MeV in 2-keV step sizes, recording the energy deposited in the crystal as a function of energy at each step. This calculation required more than 5,500 simulation runs using INL's High Performance Computing resources. The results of these calculations are shown in Figure 1. As a first-step trial of these deconvolution techniques, a standard Cs-137 check source was used to acquire a measured spectrum using the $LaBr_3$ detector. The before and after results of applying one of the tested algorithms are shown in Figure 2.

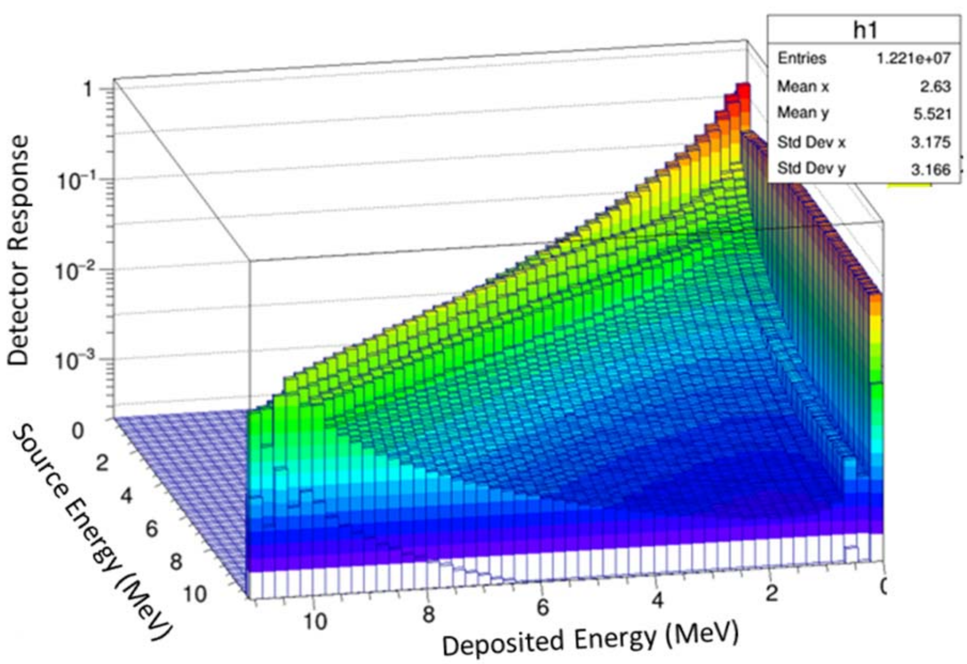


Figure 1. Calculated detector response matrix for a $LaBr_3$ detector.

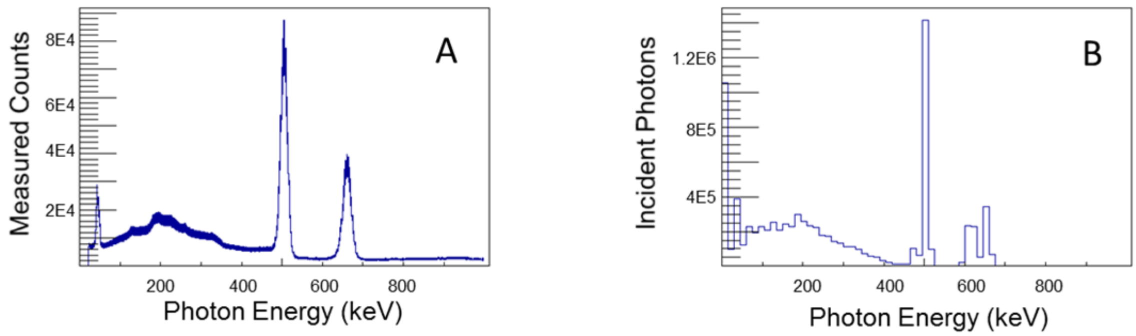


Figure 2. A before and after demonstration of one deconvolution algorithm built into ROOT. Plot A (left) is the measured spectrum from a Cs-137 source, while Plot B (right) is the incident source spectrum deconvolved from the $LaBr_3$ detector response.

Benefits to DOE

Less-expensive, high-fidelity sensors will provide increased confidence in radiation detection for nuclear nonproliferation and counterproliferation measurements related to advanced safeguards, nuclear forensics, emergency response, and nuclear material detection.

Presentations

Shy, Daniel, "A Parameter Study to Optimize Scintillator Characteristics for Increase Sensitivity in Nuclear Nonproliferation, Safeguards, and Security Based Applications," PNNL Summer Safeguards Course and Symposium, Richland, Washington, July 7–August 1, 2014.

14-075—Development of Tools and Methodologies for Uncertainty Quantification and Validation for Multiphysics Fuel Performance Simulation

Cristian Rabiti, Richard Williamson, and Anil Prinja[1]

Fuel performance analysis is characterized by a long computational time that is further complicated by generally nonlinear phenomena. Many of the parameters used in nuclear fuel behavior models are characterized by large uncertainties. Multi-physics simulations bring in additional uncertainties from other models not used in typical fuel modeling. In particular, coupling neutronics calculations with fuel performance calculations exacerbates this behavior by introducing additional nonlinearity and increasing the dimensionality of the input space. Given these complexities introduced by sophisticated modeling, the estimation of uncertainties characterizing fuel performance simulation is a difficult challenge. The goal of this LDRD is to meet this challenge.

Fortunately, only a few figures of merit are of interest to engineers. Therefore, the effective dimensionality of the input space is smaller than the total problem dimensionality. In other words, the fact that engineering decisions are made relying on a few figures of merit reduces the effective dimensionality of the input space because some combinations of variations of the input parameters exist, and some of the important figures of merit are insensitive to these variations.

These considerations suggest that reduced-order models could be positively used to replace real simulations and to propagate uncertainties. When the effective dimensionality is low, it is possible to construct mathematical models (reduced-order models) that are of a fast evaluation and to replace the original expensive models. These reduced-order models could be used to analyze the propagation of uncertainty with a very low computational time.

Part of the work covered by the LDRD is assessing which reduced-order models are most suitable for this task, how to make such determinations, and evaluating when a reduced-order model has received enough training to replace the real model in the uncertainty quantification.

Another direction of the current work sponsored by this LDRD is the application of dimensionality reduction for the evaluation of the uncertainty affecting the nuclear cross section. The cross section, when considered by isotope and on a very fine energy grid, exhibits a high degree of correlation. This correlation is expressed by the covariance matrix supplied by the experimentalists and could be used to reduce the dimensionality of the input space.

Summary

The coupling between RAVEN and BISON (fuel performance code) has been completed. The characterization of the dimensionality and nonlinearity of a prototypical fuel performance analysis has been performed. For example, a parametric study performed using BISON and RAVEN shows the degree of nonlinearity of a prototypical case in fuel performance analysis that has been presented and discussed in a journal article titled “Fuel Reliability Analysis Using BISON and RAVEN” (see Publications section below).

Following this preliminary study, the detected degree of nonlinearity seemed to be compatible with a polynomial representation, as surrogate models, of the figures of merit of interest in the multiphysics fuel performance analysis. The work has, therefore, proceeded by implementing different types of anisotropic construction of Stochastic Collocation generalized Polynomial Chaos (SCgPC), like hyperbolic cross and total degree, in RAVEN. This task has been done in cooperation with the University of New Mexico, and a student is currently working at INL implementing these methodologies as part of his Ph.D. thesis. While SCgPC represents the state

[1] University of New Mexico

of the art for uncertainty quantification, it still will not be capable of addressing the high dimensionality of the input space (e.g., cross sections) when reactor physics (neutron transport and nuclide depletion) will also be accounted for in fuel performance analysis. To overcome such challenges, two strategies are under development. First, the SCgPC is implemented adaptively (the degree of the expansion set is chosen automatically), and a new type of expansion has been tested (High Density Model Reduction) with positive results. Second, Dr. Congjiang Wang, a newly hired postdoc, is implementing an approach to reduce the dimensionality of the cross-section input space.

The covariance matrix of the cross section is decomposed using truncated-singular value decomposition. The eigenvalues of such decomposition represent the direction of a new coordinate system where the transformed cross sections are now independent. The new independent set of cross sections is smaller than the original set. This approach, applied to a pin simulation (steady-state neutron transport simulation using SCALE and TSUNAMI-2D codes), has shown a reduction of the input space from 11308 to 1110, with an error on the K_{eff} of 10 pcm.

A scheme has been proposed, and is currently being tested, where an initial reduction of the input space is performed using the techniques described above, and then the adaptive SCgPC is used in the transformed coordinate system.

Unfortunately, an input dimension space of ~1,000 is still quite large for effectively using SCgPC. A technique to further reduce this input space is currently being investigated. This technique seeks to approximately remove the linear combination of the input parameters that have no impact on the figures of merit of interest for the fuel performance analysis. This work has been submitted as a paper titled “Multistep Input Reduction for High Dimensional Uncertainty Quantification” for the next PHYSOR conference.

Benefits to DOE

Benefits from the introduction of high-fidelity simulation tools have been experienced in many other fields, and, in the last decade, DOE has invested in creation of such tools for nuclear-energy applications. The nuclear sector is highly regulated; as a consequence, it exhibits a strong inertia toward adoption of new technologies. It is clear that without a strong quantification of a new tool’s uncertainties, it will not be allowed to be licensed in the nuclear industry. This is exactly the point addressed by this proposal, and success will allow the industrial deployment of several million dollars of already invested money, generating a true benefit to the nuclear industry.

The methodologies investigated here push forward the envelope of the current state of the art in uncertainty quantification. The ongoing investigation of the propagation of uncertainties in high-dimensionality space is already above the limits of what is currently done.

The project currently supports cooperation with University of New Mexico and a postdoc appointment at INL.

Publications

Rabiti, C., J. Cogliati, G. Pastore, and A. Alfonsi, “Fuel Reliability Analysis Using BISON and RAVEN,” *International Topical Meeting on Probabilistic Safety Assessment and Analysis*, Sun Valley, Idaho, April 26-30, 2015.

Talbot, P. and A. Prinja, “Sparse Grid Stochastic Collocation Uncertainty Quantification Convergence for Multigroup Diffusion,” *Proceedings of the 2014 ANS Winter Meeting*, Anaheim, California, November 9-13, 2014.

Talbot, P. W., C. Wang, and C. Rabiti, “Multistep Input Reduction for High Dimensional Uncertainty Quantification,” *PHYSOR 2016*, Sun Valley, Idaho, May 1–5, 2016, submitted.

Presentations

Rabiti, C., P. Talbot, A. Alfonsi, and G. Pastore, “Approaches for fast uncertainty quantification in continuous problems using RAVEN,” Ohio State University, May 2015, invited talk.

Rabiti, C., P. W. Talbot, and C. Wang, “Development of tools and methodologies for uncertainty quantification and validation for the multi-physic fuel performance simulation,” DOE, Germantown, Maryland, September 22, 2015.

Copyrights

The development described in the Summary section has been implemented in the RAVEN code that is currently copyrighted to Battelle Energy Alliance, LLC.

14-098—Irradiation Effects in Uranium Dioxide

Jian Gan, Kumar Sridharan,[1] Beata Tyburska-Püschel,[1] and Jeff Terry[2]

The evolution of microstructure and properties of ceramic nuclear fuel UO_2 during neutron irradiation is crucial to current and future nuclear power plants operating globally. Despite large existing empirical databases for UO_2, there is still a lack of scientific understanding of the defect progression in this material under irradiation. The point defect growth and clustering in neutron- and ion-irradiated depleted UO_2 is being studied by advanced synchrotron-based micro extended x-ray absorption fine structure (µ-EXAFS) methods and transmission electron microscopy (TEM). In this research, the novel spatially resolved µ-EXAFS has been used for characterizing irradiation damage in UO_2. Small sample size (focused-ion beam [FIB] lamella) allows examination of highly activated materials, and the small x-ray spot size allows damage profiling as a function of depth. Combining the µ-EXAFS with ion irradiation allows multiple damage levels to be examined within the same sample and a direct comparison TEM analysis. Simulation, modeling, and data fitting are a significant part of understanding the measured extended x-ray fine structure (EXAFS) spectra.

Summary

Experimental Effort

The evolution of defects on multiple-length scales in UO_2 due to H+, He^{2+}, and krypton irradiation was studied. The experimental results have been corroborated with simulation studies to provide a detailed understanding of defect distribution from singular atoms to microstructure on the micron-length scales. Using ion-irradiation accelerator facilities at the University of Wisconsin-Madison and University of Illinois Urbana-Champagne, atomic structure and microstructural defects were introduced in the UO_2 samples. The primary experimental methods to probe the lattice structure were EXAFS measurements, with x-ray diffraction (XRD) and TEM, which provided detailed information on the type and characteristics of defects on multiple-length scales. EXAFS analysis reveals the presence of oxygen defect clusters at a uranium-oxygen distance of 1.8 Å. Similar to oxidation, UO_2 maintains its overall fluorite structure at low and intermediate radiation doses. Unlike UO_{2+x}, radiation damage in UO_2 causes an increase in the lattice parameter due to an accumulation of Frenkel defects and small clusters (see Figure 1).

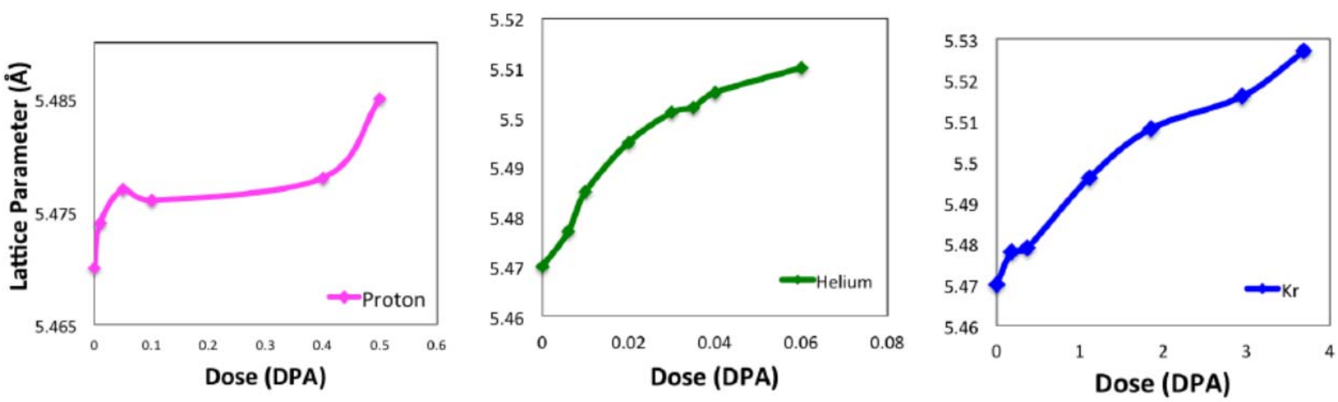


Figure 1. Increase in lattice parameter for hydrogen-, helium-, and krypton-implanted samples as a function of dose in displacements per atom (dpa).

[1] University of Wisconsin

[2] Illinois Institute of Technology

Small clusters that could not be detected at the TEM level were primarily responsible for lattice change detected by EXAFS in irradiated UO_2. Concomitant with the loss of amplitude of the crystallographic features with radiation damage, there was a significant increase in the prominence of the non-crystallographic oxygen shoulder at 1.8 to 1.9 Å from the absorbing ion by uranium. This oxygen shoulder is also seen to grow in UO_{2+x} for increasing values of 'x'. The short uranium-oxygen distance of 1.7 to 1.9 Å is characteristic of the uranyl bond, which is uranium atom double bonded with two oxygen atoms and an overall net 2+ positive charge. These bonds are highly stable in nature due to their oblate geometry and form complex molecules with actinides in used nuclear fuel storage.

The features of the spectra of the Fourier transforms are in the same positions as the crystallographic samples for all the ion doses except the highest proton ion dose. This is in agreement with historical data, indicating that UO_2 maintains its overall fluorite structure during oxidation and nuclear reactor irradiation. Lattice parameter has been shown to decrease in UO_{2+x} due to the Jahn-Teller distortion in UO_2 due to accumulation of additional oxygen interstitials in the fluorite lattice. Radiation damage, however, was shown to increase the lattice parameter in UO_2, as seen in both XRD and EXAFS experiments. This is because irradiation creates a distribution of Frenkel defects and small defect clusters that together contribute to lattice expansion with increasing ion dose. TEM measurements have been made to study larger-scale defects in irradiated UO_2 and EXAFS, and XRD measurements give insight into collective atomic defects. XRD and EXAFS measurements reveal differences in the lattice structure by a 0.5% increase in the lattice parameter, and >5% of the overall atoms fit in the UO_2 samples. Theoretical comparison between the extent of microstructure and TEM visible damage was made to local structure damage using basic mathematical calculations. This revealed that the TEM defects could potentially contribute up to 0.01% of the total damage seen in EXAFS. The remaining local structure damage is due to TEM invisible defects that contribute to the local structure variations seen in EXAFS and TEM. Therefore, it was established that the primary cause of local structure changes and lattice variations was small defect clusters—four to 30 atoms in size that cannot be seen in the TEM and cause large changes to the lattice.

Modeling Effort

The objectives of the modeling were to use cluster dynamics to describe defect cluster population in irradiated UO_2, make a connection with EXAFS characterization, and link defect data with phonon transport. During FY 2015, the cluster dynamics model was refined to simulate UO_2 irradiation conditions relevant to experiments within the project. Work proceeded on two fronts, an approach that was motivated by the EXAFS and TEM experiments. First, the cluster dynamics code was tested in the temperature range 500 to 1,000°C, a relatively low temperature range from the perspective of defect kinetics in UO_2, in order to investigate the defect behavior in a temperature range overlapping with the experimental investigations. The average cluster size and population were monitored. The balance of defects in clusters was also monitored in order to detect the off-stoichiometric state of the matrix. The latter was measured by the context of the monomers of oxygen and uranium vacancies and interstitials.

It was found that, at low temperature, the matrix tends to be hyper-stoichiometric due to the accumulation of uranium vacancies. This again adds to the controversy in the literature regarding the hyper-stoichiometric status of the UO_2 matrix under irradiation as to whether this hyper-stoichiometry is due to excess oxygen (interstitials) or uranium vacancies. Second, the off-stoichiometry limits of faulted dislocation loops in UO_2 were determined by geometric analysis of the (111) type loops. The analysis was performed by geometrically determining the maximum and minimum number of oxygen interstitials that can be added to loops for a given uranium interstitial content. It was found that the off-stoichiometry range of faulted loops in UO_2 is similar to that of voids, but the hyper-stoichiometric range was larger, indicating that loops might have more oxygen atoms on average than dictated by the 1:2 ratio of the matrix. The energy of the loops must be checked in order to pin down the off-stoichiometry range that will persist during the cluster evolution. The tendency of the loops to be more hyper-stoichiometric than hypo-stoichiometric is consistent with a previous finding that the voids (containing the opposite defects) are also more hypo-stoichiometric on average, especially at later evolution stages.

Additional progress has been made in preparing the phonon transport model to accept defect data obtained from cluster dynamics. A thorough computational assessment of phonon lifetime models and their ability to predict the mode-specific and overall thermal conductivity of UO_2 has been completed. A manuscript is currently being drafted. In FY 2016, the integration of cluster dynamics and EXAFS data into the phonon transport model will be carried out.

Benefits to DOE

The investigation of an irradiated UO_2 microstructure using both TEM and EXAFS/μ-EXAFS provides a unique opportunity to connect the lattice disorder and defect clustering to the molecular dynamics modeling simulation. INL has benefited from this work by further enhancing its R&D strength on fuel material microstructure characterization and modeling. This work has contributed to DOE's leading role on basic science research of materials behavior and performance in extreme environments. Being able to access a different facility in a different institution is critical to the success of this project. Furthermore, with the progress of the extended fuel storage option for used nuclear fuel, this research directly facilitates the understanding of the stability of UO_2 fuels following irradiation.

Publications

Gupta, M., S. Conradson, J. Pakarinen, and T. Allen, "Identification of Collective Effects in He2+ Irradiated UO2 via Extended X-ray Absorption Fine Structure Spectroscopy," in preparation.

He, L., J. Pakarinen, X. Bai, J. Gan, Y. Wang, A. EI-Azab, and T.R. Allen, "Inert Gas Measurement of Single Bubble in CeO_2," *Microscopy and Microanalysis*, Vol. 21 (Suppl. 3), pp. 751–752, 2015.

He, L., J. Pakarinen, B. Jaques, A. T. Nelson, J. Gan, A. EI-Azab, D. Butt, and T. R. Allen, "Bubble Evolution in Kr Ion Irradiated UO2 at High Temperature," to be submitted.

Khalil, Sarah, Todd Allen, and Anter El-Azab, "Off-stoichiometric cluster dynamics modeling of UO_2," *Journal of Chemical Physics*, in preparation.

Presentations

Gupta, M., "Damage Structure Evolution in Ion Irradiated UO_2," TMS Conference 2014, San Diego, California, February 18, 2014.

He, L., J. Pakarinen, X. Bai, J. Gan, Y. Wang, A. EI-Azab and T. R. Allen, "Inert Gas Measurement of Single Bubble in CeO_2" Microscopy and Microanalysis 2015, Portland, Oregon,, August 4–8, 2015.

14-104—Development of a Multiphysics Algorithm for Analyzing the Integrity of Nuclear Reactor Containment Vessels Subjected to Extreme Thermal and Overpressure Loading Conditions

Richard C. Martineau, Ben Spencer, Ray Berry, David Andrs, Hongbin Zhang, and Curtis Smith

The technical objective of this LDRD is to develop a first-of-its-kind multiscale, multiphysics algorithm for analyzing the integrity of nuclear reactor containment vessels subjected to extreme thermal and overpressure-loading conditions. The various specific physical phenomena to be considered in developing an algorithm for analyzing nuclear containment events are:

1. Single-phase, multicomponent, and multiphase flow and transport
2. Chemical reactions, including combustion, and deflagration to detonation transition
3. Shock wave formation and propagation
4. Conjugate heat transfer, including solid-state and hydrodynamic heat conduction, forced and natural convection, and radiative heat transfer.
5. Fluid-structure interaction (thermo-mechanical-hydrodynamic coupling).

The INL's MOOSE High-Performance Computing development and runtime computational framework will be utilized for this research effort. The central focus of the algorithmic R&D for this LDRD effort will take place in Bighorn, the MOOSE-based application for single- and multi-phase conjugate heat transfer. The MOOSE software repository contains some of the necessary physics modules (denoted as kernels) that are readily available for this effort. Because of the MOOSE framework's unique modular design, these kernels may be leveraged with little or no modification of the source code. Additional kernel development will be required for gas-phase chemical reactions, shock wave capture, fluid-structure interaction, and thermal radiation. Integrating these physics into a single, strongly coupled multiphysics algorithm is the research task at hand. The benefit of this algorithmic development will be delivery of a multidimensional, MOOSE-based application capable analyzing the integrity of nuclear reactor containment vessels subjected to extreme thermal and overpressure-loading conditions.

Summary

Radiative Heat Transfer

Rattlesnake[1,2] is a MOOSE-based application initially designed as a neutron transport solver. Various discretization schemes have been implemented for solving the multigroup neutron transport equation (NTE). The NTE and radiative neutron equation (RTE) share some similarities and also differ from each other. They both have the streaming direction as the independent variable. RTE has the similar time-derivative kernel, streaming kernel, collision kernel, and scattering kernel. (The name "kernel" is borrowed from the MOOSE framework, in which a kernel stands for a piece in the weak form for a particular term in the equation.) The new kernels introduced in RTE include the black-body emission kernel and the spatial varying refractive index kernels. The linear eigenvalue problem for neutron transport is solved frequently. On the other hand, RTE is typically coupled

[1] Yaqi Wang, Hongbin Zhang, and Richard C. Martineau, "Diffusion Acceleration Schemes for the Self-Adjoint Angular Flux Formulation with a Void Treatment," *Nuclear Science and Engineering*, Vol. 176, No. 2, pp. 201–225, 2014.

[2] Yaqi Wang, "Nonlinear Diffusion Acceleration for the Multigroup Transport Equation Discretized with SN and Continuous FEM with Rattlesnake," *International Conference on Mathematics, Computational Methods & Reactor Physics (M&C 2013)*, Sun Valley, Idaho, USA, May 5–9, 2013.

with the energy transfer equation in a strong nonlinear fashion. Nonlinear transient solvers are required for solving RTE. Outputs for modeling radiative heat transfer can be maximized by using Rattlesnake/MOOSE with the minimum efforts. Rattlesnake was extended for radiative heat transfer with all discretization schemes, solvers, and so on being available for solving the multigroup RTE.

The need to solve large coupled systems of equations also required optimizations to some of the internal interfaces within MOOSE itself. In particular, optimal preconditioning of the RTE system requires building many small sub-matrices of the Jacobian matrix. These individual "blocks" of the Jacobian matrix can then be used either individually or collectively to precondition the system. The existing MOOSE interfaces only allowed building one sub-matrix at a time, requiring a full "sweep" (evaluation of finite element shape functions, variables, and material properties on each element in the mesh) for each sub-matrix to be built. In a situation with N variables and M blocks to build this would require N × M sweeps. The strong coupling between variables in RTE requires building many "off-diagonal" sub-matrices so that M converges to N giving an $O(N^2)$ algorithm to build the matrices for preconditioning. To alleviate this, a new interface was added to MOOSE that allows building multiple sub-matrices in one pass through the mesh, effectively reducing the computational complexity to O(N).

The implementation of RTE in Rattlesnake has been tested with few benchmark problems, including the nonequilibrium Marshak wave problem, a one-group coupled problem obtained from Reference 3 with the project's SAAF-SN-CFEM transport scheme (i.e., self-adjoint angular flux with discrete ordinates method and continuous finite element method). Here, only part of the results for the nonequilibrium Marshak wave problem will be shown. Others, including results for the other benchmark problem, can be found in the detailed report, *Radiative Heat Transfer with Rattlesnake*.[3] The problem was proposed by Pomraning[4] and its solution is later extended by Su and Olson.[5] Details about this problem can be found in the articles listed in Footnotes 2 and 3. In simulations conducted for this project, the medium was finite size, and the vacuum boundary condition was applied on the new boundary. The parameters were set properly so that the variables delivered by Rattlesnake, radiation energy density and total thermal radiation emission, are directly the variables in the problems. The initial time step size was set to 10^{-18} seconds. At the first time step, the mesh was adapted so that no oscillations in the solution would be observed, which results in 233 elements mostly refined at the boundary with the non-zero incoming flux. Both spatial adaptivity and time adaptivity were turned on with the *Transient* executioner in MOOSE. The time stepper in use was *SolutionTimeAdaptiveDT*, and the error indicator was *GradientJumpIndicator*, with the refinement fraction being 0.01 and coarsening fraction being 0.5. The simulation is completed in 827 steps at time equal to 0.001 seconds. Because the calculation was done with the finite domain, the reference solution cannot be reproduced exactly. However, the boundary effect to the solutions on the left boundary is small, so a meaningful comparison to the reference solution there can still be made. The results are showed in Table 1. While the solutions are indeed close, a consistent lower solution in the simulation can be observed due to the finite domain size.

Future work includes:

1. Adding more tests and benchmark problems to verify the implementation
2. Adding material data or the cross sections with existing high-resolution spectroscopic databases

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[3] This document, written by Yaqi Wang at INL (October 30, 2014), has not been formally published.

[4] G. C. Pomraning, "The non-equilibrium Marshak wave problem," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 21, No. 3, pp. 249–261, 1979.

[5] Bingjing Su and Gordon L. Olson, "Benchmark Results for the Non-Equilibrium Marshak Diffusion Problem," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 56, No. 3, pp. 337–351, 1996.

3. Creating a more realistic benchmark for analyzing the integrity of the nuclear reactor containment vessels subjected to extreme thermal and over-pressure loading conditions.

Table 1. Solutions of the Marshak wave problem at the left boundary with $e = 0.1$.

t	$u(x = 0, t)$		$v(x = 0, t)$	
	$z_{max} = 20$, Rattlesnake	$z_{max} =$ ¥, Reference	$z_{max} = 20$, Rattlesnake	$z_{max} =$ ¥, Reference
0.001	0.08988	0.09039	0.00006	0.00006
0.003	0.14686	0.14768	0.00031	0.00030
0.01	0.23931	0.23997	0.00171	0.00170
0.03	0.34235	0.34328	0.00766	0.00762
0.1	0.43768	0.43876	0.03452	0.03446
0.3	0.48526	0.48556	0.11298	0.11322
1	0.55141	0.55182	0.31848	0.32030
3	0.66212	0.66334	0.58561	0.58906
10	0.79215	0.79420	0.78045	0.78318
30	0.87612	0.87731	0.87395	0.87523
100	0.93169	0.93202	0.93135	0.93167

Customized IAPWS-95 Water-Steam Equation of State

For the simulation of extreme thermal and over-pressure loading conditions in nuclear reactor containment vessels, especially involving single- and two-phase flows, accurate equations of state, such as the International Association for the Properties of Water and Steam package (IAPWS-95), must be used. For such computer processing unit-intensive numerical simulations, thermodynamic and transport properties of steam and water must be calculated extremely often. For the fully nonequilibrium, two-pressure, two-phase, seven-equation model, these properties must be evaluated for each phase in the *equilibrium* and in the *metastable* states.

The dependent properties of the seven-equation model are effectively the specific volume for each k-phase, v_k, and the specific internal energy for each k-phase, e_k, where k indicates the phases water or steam. Determining properties as a function of (v_k, e_k) from IAPWS-95 requires backward functions (inversions) for calculations from phasic pressure and specific volume (p_k, v_k) and specific internal energy and specific entropy (e_k, s_k). An iterative solution is required that is very time-consuming and computationally inefficient. To provide fast and accurate property calculation algorithms, INL researchers worked with researchers at the Zittau/Goerlitz University of Applied Sciences (Germany) to modify their Spline-Based Table-Look-up (SBTL) method to give properties for both water and steam phases in the equilibrium and metastable (nonequilibrium) states.[6] The SBTL method represents property functions as locally defined two-dimensional bi-quadratic polynomial spline functions of specialized transformed independent variables ($\underline{v}_k$, $\underline{e}_k$). This, along with a rapid search algorithm, allows the SBTL method to minimize the computing time and to optimize the look-up table for the desired accuracy.

[6] M. Kunick, “Fast Calculation of Thermophysical Properties in Extensive Process Simulations with the Spline-Based Table Look-up (SBTL) Method,” VDI Fortschritt-Berichte, Germany, 2015, in preparation.

The SBTL method was demonstrated at INL, with small-scale test harness computational fluid dynamics codes, to be capable of reproducing the IAPWS-95 equation of state properties with high accuracy and significantly reduced computational times for both equilibrium and metastable nonequilibrium flows.

Multiphysics with MOOSE MultiApps

To improve the full core simulation fidelity, several enhancements were added to the framework. These improvements include improved "Multiapps" integration, more robust "Transfers," new transfer types, and refactored stepping and time control. The Multiapps System[7] was redesigned to better support multilevel simulations with support for restart and recovery for long-running simulations. The new system is now capable of saving checkpoints throughout the Multiapps hierarchy, which can restore the state of a simulation up to a valid state due to planned or unplanned termination. This capability can be used to resume an application to simulate different end-state scenarios or to simply resume a simulation for any reason due to hardware faults or incorrect input file parameters. Transfers have been made far more robust, providing better behavior under complex parallel decompositions while providing better user diagnostics when failures occur. Additionally, new transfer types have been added to the framework, giving simulation designers even more choices for transferring field data among various applications under the MOOSE framework. Finally, the MOOSE executioners were refactored to incorporate an improved hierarchical stepping scheme. The new system provides a consistent interface for a wide variety of solve strategies ranging from simple steady-state solves, normal transient solves with adaptivity, or even complex power-iteration with Picard iteration steps. These new capabilities at the framework level enable MOOSE to solve tightly coupled systems of fully-coupled equations for the first time. Previously, MOOSE was best suited for fully coupled simulations or loosely coupled systems of fully coupled equations.

Benefits to DOE

This work is directed to create a new algorithm for thermal-mechanical, fluid-structure interaction to address structural integrity in the presence of thermal radiation, natural and forced convection, and strong hydrodynamic forces. While this effort is directed with nuclear safety for nuclear power plants in mind, applications for nuclear security are numerous.

Presentations

Wang, Yaqi and N. Gleicher, "Revisit Boundary Conditions for the Self-Adjoint Angular Flux Formulation," PHYSOR 2014 - The Role of Reactor Physics toward a Sustainable Future, Kyoto, Japan, September 28-October 3, 2014.

[7] D. R. Gaston, C. J. Permann, J. W. Peterson, A. E. Slaughter, D. Andrs, Y. Wang, M. P. Short, D. M. Perez, M. R. Tonks, J. Ortensi, and R.C. Martineau, "Physics-based multiscale coupling for full core nuclear reactor simulation," *Annals of Nuclear Energy*, October 2015.

15-002—Experimental Scenarios of Adversity and Recovery in Aqueous Separations

Peter Zalupski and Travis Grimes

This project focuses on demonstrating the value of an instrumental capability called AKUFVE, which is a Swedish abbreviation that stands for "apparatus for continuous measurement of distribution factors in solvent extraction." The capability is specifically designed as a closed, recirculating system of two equilibrating, immiscible liquid phases. To fully capitalize on AKUFVE's design, the movement of solutes across the liquid-liquid boundary must be monitored. Accordingly, the recirculating unit must be equipped with dynamic flow cells designed to track the partitioning of detectable ingredients in a two-phase environment. This LDRD project targets the development of a state-of-the-art online monitoring apparatus, with AKUFVE as the "heart" of the system, surrounded by spectrophotometric and radiometric detection capabilities. This unique design will offer opportunities to mimic the experimental scenarios of adversity and recovery in aqueous separations, where various liquid-liquid formulations are perturbed to seek advantages in resource recovery.

Summary

AKUFVE couples the utility of a one-stage, centrifugal mixer-settler unit with the convenience of an accessible flow-through design to allow sample diversion/addition and in-line measurements of physico-chemical properties of liquid phases present in the experiment. Figure 1 is a conceptualized graphical representation of the AKUFVE design. The two immiscible liquid phases, delivered inside the dynamic mixer chamber, are equilibrated to facilitate the mass transfer. The continuous H-centrifuge with a flow-regulating system affords a rapid, efficient phase separation. The auxiliary flow system is equipped with a diverting valve, a flow meter, and a pressure gage for light and heavy phases, allowing for continuous measurements of choice. The operation of AKUFVE is based on a mix-separate-sample loop, and the mass balance equilibrium may be monitored spectroscopically as it responds to various stimuli (additives, temperature, speed of mixing, diversion, etc.). The high flow rates generated by this system (~500 mL/min) ensure fast attainment of an equilibrium, which when perturbed is quickly reestablished, enabling new measurements. As a result, a large amount of thermodynamic data sets may be collected to facilitate various tasks, beginning with drafting a preliminary profile of a separation concept and ending with a complete thermodynamic assessment of solute distribution to design a theoretical model of a separation process.

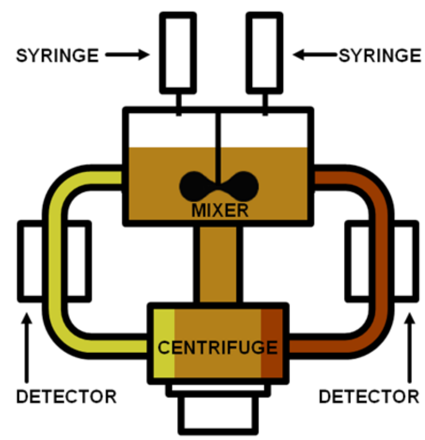

Figure 1. Illustration of two immiscible liquid phases delivered inside the AKUFVE mixer chamber and then equilibrated to facilitate mass transfer.

Initial FY 2015 project deliverables were as follows:

1. A mini-AKUFVE dynamic-mixer/centrifugal-separator (ADMCS-10) unit was built by Metallextraktion AB (Sweden) according to U.S. codes and regulations and delivered to INL
2. A laboratory was tailored to meet the operating requirements of AKUFVE
3. QEPro spectrophotometers equipped with a deuterium-tungsten light source were procured from Ocean Optics, Inc.
4. LaBr(Ce) scintillation detectors, together with digiBASE photomultiplier tube spectroscopy electronics, were procured from AMETEK
5. The utility of LabVIEW is being evaluated as a communications platform.

Benefits to DOE

This project attempts to expand the horizons of the experimental research portfolio of the aqueous separations activities at INL. The new experimental capability, which allows for a dynamic means of monitoring liquid-liquid partitioning equilibria, could be an important asset not only to fundamental research in aqueous separations but also when supporting programmatic testing of processes (e.g., providing valuable data in support of the identification of the reference flowsheet).

15-013—Simulation-Based Analysis of Procedures and Accident-Management Guidelines

Curtis Smith, Tony Koonce, Ronald Boring, and Robert Youngblood

The objective of the LDRD is to improve the state of the art of probabilistic risk analysis (PRA) by modeling plant logic, procedures, and accident-management guidelines in a unified way using recently developed simulation tools in the MOOSE suite. Existing fault-tree/event-tree risk models address human performance in a largely ad hoc way; incorporating a complete set of procedures and guidelines into a simulation model of plant risk is well beyond the state of practice. This research aims to advance the technical basis for enabling implementation of simulation-driven predictive severe accident management guidelines as a means to address uncertainty in the selection of actions by projecting the effect of those actions into the future. To help reach this goal, the proposed project will investigate the feasibility of a computerized online decision-support system for risk-informed management of beyond design basis accidents. Using RAVEN, the project will forecast decision-support options (for plant operators) from a large spectrum of simulation-based scenarios. The novel aspect of the work is inclusion of a comprehensive set of procedures and accident-management guidelines in a simulation model of plant performance. This is important technically because, despite decades of work on human reliability methods for PRA, procedurally mandated actions still surprise observers (e.g., shutting off high-pressure injection at Three-Mile Island and shutting off the isolation condenser at Fukushima), partly because of the ad hoc and generally incomplete treatment of human performance in state-of-practice PRA.

Summary

The LDRD team kicked off this project in November 2014 by interacting with the ATR operations staff. ATR training staff briefed the LDRD team on expectations of operators upon alarm indications being received and different training scenarios performed in the simulator. The ATR training staff also provided insights regarding the current thermal analysis used by ATR and its interface to the simulator. The ATR training staff also presented a few events and associated emergency procedures that would be appropriate for Phase 1 applications.

The LDRD team reviewed the various events and emergency procedures recommended by ATR personnel. The team decided to pursue the loss-of-primary-coolant, flow-initiating event and its impacts on E-0, "Entry Procedure," and then the transitions into subsequent emergency procedures. The team used this event to develop the simulation methodology that will be used throughout this LDRD project.

The team's simulation methodology (Figure 1) was designed to closely resemble the reality of an operating nuclear plant by actively modeling the various attributes that constitute the as-built and as-operated plant. The as-built aspect of the plant is included in the simulation by incorporating the plant's thermal-hydraulic model, equipment reliability data for plant components, and plant indications and alarms. Plant personnel and procedures make up the as-operated aspect within the simulation framework. The as-operated plant analysis is the unique aspect of the simulation model. It only includes approved, documented operating procedures for the plant.

The simulation code is currently being written in the language Python to facilitate its interface with RAVEN. RAVEN will act as the coordinator between the simulation code and RELAP-5, the current TH code for ATR. As the simulation code makes steps in time, any operator action in accordance with approved procedures that alters the state of a plant component is relayed to RELAP-5 through RAVEN. The component change of state is then included in the TH calculations for the simulation. The simulation ends if plant conditions are stabilized by the operators' actions or if a surrogate value that indicates core damage is reached.

The team has developed the modeling methodology that will be used in order to simulate operator actions while implementing mitigating procedures for initiating events for ATR. The team continues to develop the simulation code; code libraries continue to be populated with plant procedures, components, indications, and operator actions. RELAP-5 is the selected thermal-hydraulic software for this project in order to take advantage of the current ATR modeling done in the code, and the physical analysis of the plant will be done within the MOOSE software suite.

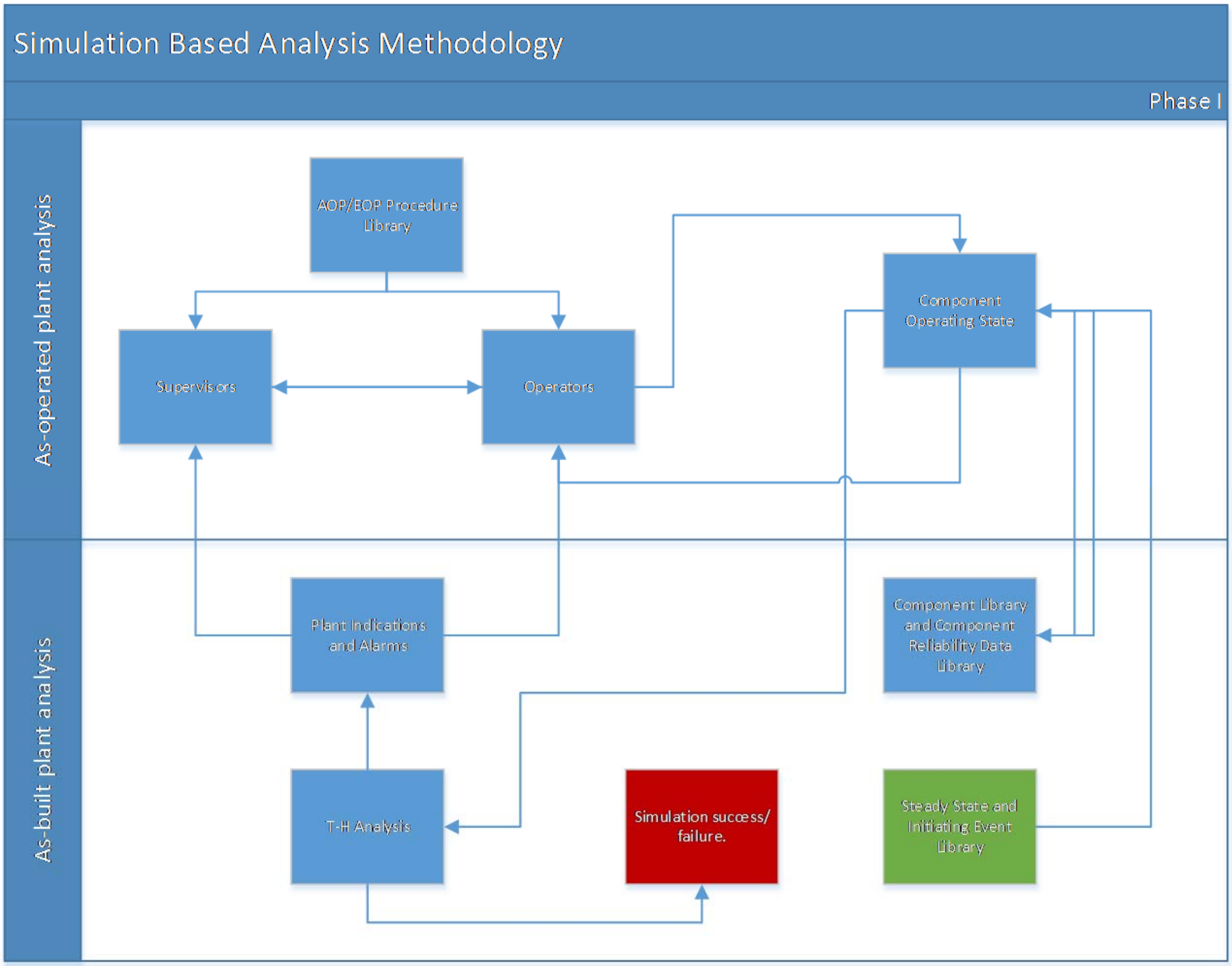

Figure 1. Simulation-based analysis methodology.

Benefits to DOE

The capability to be developed has the potential to materially improve the state of practice of PRA, affecting facilities at INL and elsewhere and promoting work for INL staff. INL will benefit by the latest developments in PRA using the capabilities of MOOSE.

The research is being performed using ATR as the case study. Upon proof-of-principle, the technique could be used by the nuclear industry and regulators alike, specifically including the Light-Water Reactor Simulation program. The research will also lead to development of a new capability within the MOOSE suite. There is also some potential for expanding the methodology beyond the nuclear industry and adapting it to other low-probability/high-consequence industries and infrastructures.

15-014—^{135}Cs Quantification: A ^{135}Xe Proxy

Darin Snyder, Mathew Snow, Mary Adamic, and Nick Mann

In support of an existing relationship with the Comprehensive Nuclear-Test-Ban Treaty Organization, measurements of ^{135}Xe activities are regularly performed on air samples collected in association with suspected nuclear detonations. This research assesses the viability of ^{135}Cs measurements by thermal ionization mass spectrometry as a tool to estimate the quantity of "decayed" ^{135}Xe in air samples. The relatively short half-life of ^{135}Xe (~9 hours) can make its quantification logistically difficult for samples taken in far-field locations. The scenario in which this tool would be useful is one in which air or particulate material containing ^{135}Xe (or its parent isotope ^{135}I, Figure 1) had been collected, but then sufficient time elapsed prior to ^{135}Xe activity measurement, allowing the ^{135}Xe activity to fall below current limits of detection. Measurement of the ^{135}Cs content of such samples allows an accurate assessment of the original ^{135}Xe content of the samples because ^{135}Cs is the daughter product of ^{135}Xe. The ultratrace analysis team at INL has developed a technique to quantify the ^{135}Cs/^{137}Cs ratio of femtogram levels of fission-product cesium from environmental matrices (e.g., soils, vegetation, and air filters). This tool provides the ability to distinguish between environmentally distributed ^{137}Cs derived from nuclear detonations (fast fission) versus that derived from power reactors—either operating reactors or fuel-processing facilities (thermal fission). Expanding this technology to the problem area described above requires a better understanding of the potential role of chemical fractionation among the precursor isotopes of cesium (i.e., iodine and xenon) during atmospheric transport and how this might quantitatively affect estimates of original xenon content based on cesium measurements. Additionally, improvement of the current analytical sensitivity provided by thermal ionization mass spectrometry will be critical in the development of this tool. The existing method provides a limit of detection (LOD) for ^{135}Cs of 2.5E7 atoms derived from soil matrices. This LOD is a conservative estimate with respect to the cesium derived from air samples because the matrix associated with the cesium derived from collection spheres or air filters (Figure 2) will be far less complex than that of soils. Therefore, the ^{135}Cs LOD for spheres is anticipated to be significantly reduced. Application of this technology may provide a solution to a particular identified problem within the nuclear nonproliferation community.

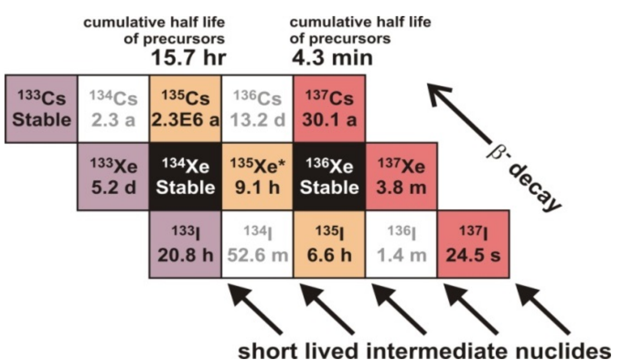

Figure 1. A portion of the chart of the nuclides spanning the 133–137 mass range. The half-life of each of the nuclides is at the bottom of each box. ^{135}Cs grows in via β decay and is the relatively long-lived daughter product of ^{135}Xe. ^{135}Cs is essentially stable over the timescales of interest to this work and as such can theoretically be used to quantify the amount of ^{135}Xe present in an air sample collected weeks or even years prior to the time of measurement.

Figure 2. One type of sample media being investigated is the RASA-type air filter. Shown here is the RASA prior to sectioning and chemical processing. This sample medium will contain particulate material along with adsorbed cesium and iodine species.

Summary

During the first eight months of this project, work was divided between two primary tasks. Task 1 was focused on identifying and assessing the appropriate sample matrices such that iodine and cesium measurements from a real-world setting could be made. Task 2 involved the development of a chemical-separation and -purification procedure for the matrix of interest that would allow for quantitative recoveries of iodine and cesium. With respect to Task 1, a partnership with researchers at Health Canada, Canadian Radiological Monitoring Network (Kurt Ungar), has been established. Radionuclide Aerosol Sampler/Analyzer (RASA)-type air filters were collected from various locations in North America (Figure 3) in the days following the Fukushima-Diiachi nuclear accident in 2011 in Japan. ^{137}Cs activities on some of these filters have shown slight elevations above background. Radioxenon (Xe-131m, Xe-133, and Xe-133m) and radioiodine (I-133) measurements were co-located with these air samplers and, combined with the RASA air filters, provide a unique sample array by which chemical fractionation among iodine-xenon-cesium decay chains can be assessed once the ^{135}Cs/^{137}Cs ratios are quantified. Gaining an understanding of this potential role of chemical fraction will be a critical component in the application of this tool to real-world samples.

Figure 3. RASA-type air filter samples have been secured as a part of a research partnership between INL and Health Canada, Canadian Radiological Monitoring Network. These air filters were exposed during the days and weeks following the Fukushima-Diiachi nuclear accident in Japan. Some of the filters show elevated ^{137}Cs activities. Short-lived radioxenon measurements were made on air samples at the same time and location as the filter collections, allowing for the assessment of the role of chemical fractionation among iodine-xenon-cesium decay chains during atmospheric transport.

With respect to Task 2, significant effort in FY 2015 has been dedicated to the development of a robust method for the isolation and purification of iodine and cesium from this sample matrix. Expertise from INL's accelerator mass spectrometry team has been leveraged to assist with this effort. With the chemical extraction/separation method in place, nine filters have been subsampled, and iodine has been recovered via a 5% tetramethyl ammonium hydroxide leach. These filter residues have been set aside for cesium recovery and purification via the project's standard microwave digestion – ion chromatographic separation method. Analyses of the ^{129}I/^{127}I and ^{135}Cs/^{137}Cs ratios will be made by accelerator mass spectrometry and thermal ionization mass spectrometry, respectively. These data combined with the previous measurements of the short-lived ^{135}Xe activity at the time of collection (April 2011) will allow a quantitative assessment of the role of chemical fractionation to be made.

Benefits to DOE

A primary component of DOE's nuclear nonproliferation mission, as administered through the Office of Defense Nuclear Nonproliferation, develops and tests new technologies to advance U.S. capabilities to monitor nonproliferation and arms-control treaty and agreement implementation, provides unique training and capacity-building programs, and engages internationally to promote nonproliferation norms and best practices through bilateral and multilateral work. The International Atomic Energy Agency is a core partner in these efforts. This research directly supports this mission area through the development of a new technological capability that expands the U.S. capability to assess and evaluate potential nuclear events.

15-023—Development of Stochastic 3D Soil Response Capability in MOOSE to Provide Design and Beyond-Design-Basis Seismic Motions for Nuclear Facilities

Justin Coleman, Swetha Veeraraghavan, and Jacobo Bielak[1]

The MOOSE framework can be used to develop a structural dynamics capability for performing stochastic site-response analyses. The structural dynamic capabilities can be used for seismic analysis, as well as other dynamic events such as fuel rod vibration in reactor cores.

Summary

Dynamic problems like the response of a multi-degree-of-freedom structure to external forcing and wave propagation in a medium can be solved using the Tensor Mechanics module in MOOSE. Rayleigh damping and numerical damping using the Hilber-Hughes-Taylor (HHT) time-integration scheme are the new additions to the structural dynamics capabilities in MOOSE.

The equation of motion for a typical dynamics problem has the following format:

$$M\ddot{u} + C\dot{u} + Ku = F_{ext} \tag{1}$$

Here, M, C, and K are the mass, damping, and stiffness matrices, respectively, and F_{ext} is the vector of external forces at the nodal points; $u, \dot{u},$ and $\ddot{u}$ are the vector of displacement, velocity, and acceleration at the nodal points, respectively.

The most common form of damping used in dynamics is Rayleigh damping. The damping matrix is expressed as a linear combination of the mass and stiffness matrices, i.e., $C = \eta M + \zeta K$. Here, η and ζ are the mass- and stiffness-dependent Rayleigh damping parameters, respectively.

The goal is to solve the above equation for the displacements (u) as a function of time. A time-integration scheme is required for achieving this goal. Newmark-beta and HHT time-integration schemes are two of the commonly used methods in dynamics.

Using the Newmark-beta time-integration method, the acceleration and velocity at time $t + \Delta t$ are expressed in terms of the displacement, velocity, and acceleration at the previous time step (t) and the displacement at $t + \Delta t$.

$$\ddot{u}(t + \Delta t) = \frac{u(t+\Delta t) - u(t)}{\beta \Delta t^2} - \frac{\dot{u}(t)}{\beta \Delta t} + \frac{\beta - 0.5}{\beta}\,\ddot{u}(t) \tag{2}$$

$$\dot{u}(t + \Delta t) = \dot{u}(t) + (1 - \gamma)\Delta t \ddot{u}(t) + \gamma \Delta t \ddot{u}(t + \Delta t) \tag{3}$$

In the above equations, β and γ are the Newmark-beta time-integration parameters. Substituting the above time-integration equations into the equation of motion (Equation 1) will result in a linear system of equations of the form $Au(t + \Delta t) = b$ from which $u(t + \Delta t)$ can be calculated.

The HHT time-integration method is built on the Newmark-beta method. In addition to the Newmark-beta equations, the equation of motion is also altered to obtain:

$$M\ddot{u}(t + \Delta t) + (\eta M + \zeta K)[(1 + \alpha)\dot{u}(t + \Delta t) - \alpha \dot{u}(t)] + K[(1 + \alpha)u(t + \Delta t) - \alpha u(t)] = F_{ext}(t + \alpha \Delta t) \tag{4}$$

[1] Carnegie Mellon University

Here, α is the HHT time-integration parameter. This algorithm is stable for $-\frac{1}{3} \leq \alpha \leq 0$, $\beta = \frac{(1-\alpha)^2}{4}$ and $\gamma = \frac{1-2\alpha}{2}$.

To implement these methods in MOOSE, the equation of motion has to be converted to a different format because MOOSE does not create and store mass and stiffness matrices. The modified equation of motion is:

$$\rho\ddot{u}(t+\Delta t) + \eta\rho[(1+\alpha)\dot{u}(t+\Delta t) - \dot{u}(t)] + \zeta\nabla \cdot \left[(1+\alpha)\frac{d}{dt}\sigma(t+\Delta t) - \alpha\frac{d}{dt}\sigma(t)\right] + \nabla.[(1+\alpha)\sigma(t+\Delta t) - \alpha\sigma(t)] = F_{ext}(t+\alpha\Delta t) \quad (5)$$

Here, ρ is the density of the material, σ is the stress tensor, and $\nabla \cdot$ is the divergence operator. The contribution of the first two terms involving ρ is calculated in InertialForce.C, and the contribution from the next two terms involving stress is calculated in DynamicStressDivergence.C located in moose/modules/tensor_mechanics/src/kernels/.

Comparing the results from MOOSE for a wave-propagation problem with ABAQUS (a commercial FEM software package) validates the above additions to MOOSE. For this comparison, the shear wave propagation along a soil column is modeled, and the displacement at the free surface is obtained when a displacement time history is applied to the bottom of the soil column, as shown in Figure 1. A soil column of height (*H*) 25 m with uniform shear wave velocity (V_s) of 100 m/s is chosen. The soil column is modeled in MOOSE and ABAQUS using 100 solid brick elements (along the height of the column), and it is constrained to move only in the direction of input displacement in order to simulate one-dimensional shear wave propagation. Rayleigh damping parameters η and ζ are set to 0.1, and HHT time-integration parameters $\alpha = -0.3, \beta = 0.4225$ and $\gamma = 0.8$ are used in both MOOSE and ABAQUS for this analysis.

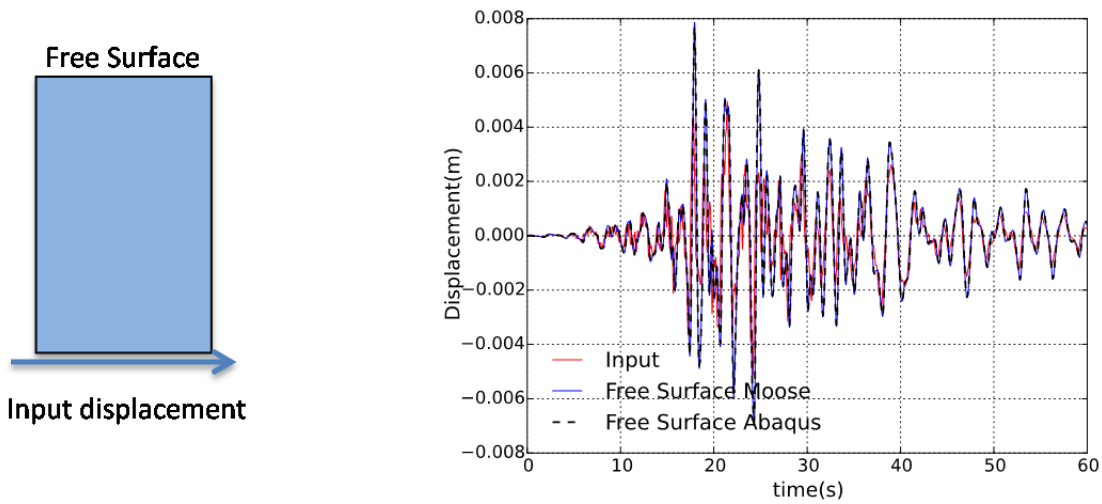

Figure 1. Soil column on left and output on right with comparison between MOOSE and ABAQUS.

In Figure 1, the input-displacement time history and free-surface time history given by MOOSE and ABAQUS are plotted. The results from MOOSE agree well with those from ABAQUS. The input displacement is amplified due to the presence of the soil column. The 5% damped displacement response spectra shown are Figure 2 clearly shows this amplification.

Benefits to DOE

The commercial nuclear industry is constantly dealing with seismic-related concerns. For instance, the nuclear industry is currently addressing the Near-Term Task Force recommendations.

The first Near-Term Task Force recommendation dealing with seismic and flooding, Recommendation 2.1, states, “Order licensees to reevaluate the seismic and flooding hazards at their sites against *current NRC requirements and guidance, and if necessary, update the design basis and SSCs important to safety to protect against the updated hazards*.” Developing a structural dynamics capability using MOOSE to model seismic wave propagation provides access to other numerical physics so that virtual nuclear power plants can be tested with virtual earthquakes. This will allow nuclear power plant owners identify potential issues and resolve them.

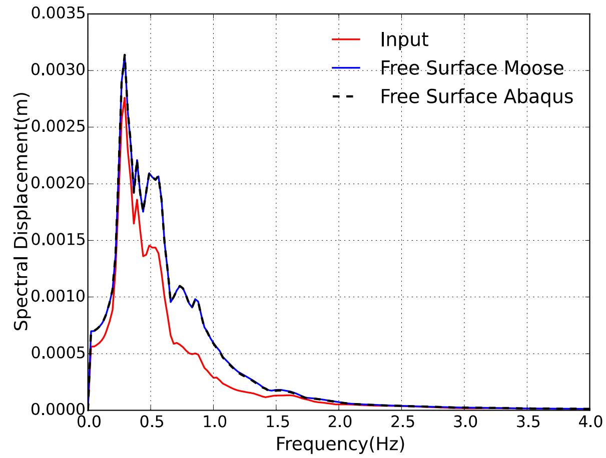

Figure 2. Percent damped displacement response spectra.

15-032—Development of New Method for High-Temperature Thermal-Conductivity Measurements of Nuclear Materials

Krzysztof Gofryk, Robert Mariani, and Michael Tonks[1]

The thermal conductivity of nuclear fuels governs the conversion of heat produced from fission events into electricity, and it is an important parameter in reactor design and safety. Different scattering mechanisms affect thermal conductivity at different temperatures. Therefore, to fully understand and reliably model this property, it is crucial to study the thermal conductivity in a broad temperature range. However, black-body infrared radiation makes this task challenging above room temperature, and several transient techniques have been developed to overcome this issue. The objective of this LDRD is to extend the measurement capability of the project's new state-of-the-art Physical Property Measurement System experimental setup from 350 to 800 K using the so-called 3ω (omega) method. This technique is considered to be the best pseudo-contact method available and enables direct measurement of thermal conductivity of very small samples. This is rare for transient thermal transport measurements because independent determinations of the thermal diffusivity and heat capacity are required to derive the thermal conductivity. In addition, this technique has intrinsically the lowest possible errors caused by the infrared radiation, and the error-term arising from radiation is estimated to be less than 2% even at 1,000 K. The adaptation of this method will be novel for nuclear materials. The new experimental setup will allow study of the thermal conductivity of small samples of nuclear materials in exceptionally broad temperature range (2-800 K), and the data obtained will help to advance the theoretical understanding and modeling of reactor fuel and future fuel development.

Summary

The main goal of the project is to develop a new method for thermal conductivity measurements of nuclear materials using the 3ω method.

Accomplishments during the first year of the project include the following:

- Prepared a DynaCool-9 experimental setup for the 3ω method development and implementation. In particular, the project purchased and adapted a Quantum Design Multi-Function Probe for the development. The probe has been installed and tested.
- Purchased all necessary equipment such as electronics (nano-voltmeter, *ac* current source, lock-in amplifier, etc.), laboratory computer, LabView software, and optical microscope.
- Performed high-resolution thermal conductivity measurements of selected reference samples (SiO_2, UO_2, etc.) using the thermal transport option. Figure 1 shows the experimental configuration used for the thermal conductivity measurements (both steady-state and pulse-power methods). The results obtained will serve as reference and calibration data for the 3ω technique
- Hired an experienced postdoc from the University of Houston to work on the project.

Figure 1. SiO_2 testing sample mounted on thermal transport option probe ready for thermal conductivity measurements.

[1] Current affiliation: Pennsylvania State University

In addition, one summer intern from the University of New Mexico worked on this project. His research was related to thermal conductivity measurements and software development. He presented a poster titled “Impact of different scattering mechanism on thermal conductivity” during the INL Intern Final Project Showcase.

Benefits to DOE

Thermal conductivity is a key engineering parameter in the conversion of heat produced by fission events to electricity. Therefore, new reliable methods for thermal conductivity determinations of nuclear materials, such as the 3ω technique, together with advanced modeling, are key parameters in understanding and developing new nuclear fuels, leading to more efficient energy production and better security for the nation. While developed for small bulk samples, this method may also be applied for micro-size and thin-film materials, which is unique and can be extended in the future to active materials such as neptunium-, plutonium-, and americium-based phases. In addition, this *ac* thermal conductivity method could be also modified to measure *ac* Seebeck coefficient (2ω-method) and heat capacity. This cutting-edge research will help INL maintain a leading position in nuclear fuel research.

Presentations

Gofryk, K., et al., “Spin-phonon interactions to control the thermal transport in uranium dioxide,” American Physical Society meeting, San Antonio, Texas, March 2015.

Meng, J. and K. Gofryk, “Impact of different scattering mechanism on thermal conductivity,” INL Intern Final Project Showcase, INL, August 2015.

15-039—Transient Modeling of Integrated Nuclear Energy Systems with Thermal Energy Storage and Component Aging and Preliminary Model Validation via Experiment

Shannon M. Bragg-Sitton, J. Michael Doster,[1] Steve Terry,[1] Carol Smidts,[2] Andrew Klein,[3] Qiao Wu,[3] Julie Tucker,[3] Charles Forsberg,[4] and Patrick McDaniel[5]

Nuclear power systems are proposed as a means of offsetting intermittent generation sources, such as wind and solar, via tight, behind-the-grid coupling. It is desirable to operate nuclear systems at or near baseload capacity; hence, thermal and electric energy storage technologies are being investigated for potential coupling to nuclear heat sources to maximize reactor utilization while providing electric and thermal energy resources. Steam diversion in a nuclear hybrid energy system (NHES) to thermal storage or other applications will initiate a reactor transient due to tight system coupling. There is a need to develop validated modeling tools to adequately characterize coupled system response in combination with operational strategies, control algorithms to optimize for transient maneuvers, and address potential impacts of degrading component health. This project includes modeling of potential electric and thermal energy storage systems integrated with nuclear systems, modeling of anticipated transient behavior/response of subsystems, conducting limited experiments and mining existing data to validate these models, and assessing the impact of aging and degradation of key components (e.g., valves) on system operation. Also being conducted are preliminary investigations of advanced energy-conversion systems that could be coupled with advanced-reactor technologies as an evolutionary application for nuclear energy to advanced hybrid systems.

Summary

In FY 2015 the North Carolina State University model for an integral pressurized-water reactor was modified for use in hybrid applications, allowing simulation of baseload and load following operation and diversion of steam and electric power during off-peak electrical demand. Models for chilled-water and compressed-air energy storage have been completed, and modeling of a steam accumulator bank has been initiated. A novel Firebrick Resistance-Heated Energy Storage (FIRES) technology investigated by the Massachusetts Institute of Technology could offer an electrical-to-thermal storage option to improve the overall efficiency and economic performance of a hybrid system. Market studies to determine the potential impact of FIRES are under way, and preliminary system designs are being developed. Researchers at Oregon State University have identified and compiled relevant test data from the Multi-Application Light Water Reactor Test Facility that will be used for initial model validation. Data include steady operation (natural circulation) at various core powers, transition between power levels, and a loss-of-feedwater accident, including reactor blowdown, containment condensation, and cooling pool heat exchange. A corresponding RELAP5-3D model of the Multi-Application Light Water Reactor Test Facility is being updated. FY 2015 work at Ohio State University included initial development of (a) the underlying concepts and prototype tools for a distributed test bed for the verification and validation of NHES and (b) an online monitoring system for components that may suffer unusual aging due to their increased use in a nuclear hybrid configuration. A key accomplishment includes development of a method to determine the probability that a control system that is distributed within a network is stable. The capability to predict system stability enables dynamic allocation of software components to different physical locations to maximize system stability.

[1] North Carolina State University
[2] Ohio State University
[3] Oregon State University
[4] Massachusetts Institute of Technology
[5] University of New Mexico

Progress was also made toward NHES applications. A supercritical CO_2 (S-CO_2) corrosion test facility has been designed and constructed at Oregon State University with partial support from the INL LDRD, and initial corrosion experiments are now under way to assess performance of multiple candidate alloys. Data from these tests will support design of an S-CO_2 cycle that could be incorporated in future hybrid system design. Upgrades to the Nuclear Air-Brayton Combined Cycle and Recuperated Cycle codes at the University of New Mexico will also allow enhanced analysis capability to support the design of power-conversion systems that could be coupled with advanced-reactor technologies to improve system efficiency.

The FY 2015, project work supported the research of five undergraduate and 14 graduate students, in whole or in part, at five universities and has resulted in six peer-reviewed conference publications, three articles ready for journal submission, and one patent application. FY 2015 LDRD-supported research also led to a 2015 DOE Nuclear Energy University Program Award at Oregon State University: J. Tucker, "Advancement of Supercritical Carbon Dioxide Technology through Round Robin Testing and Fundamental Modeling."

Benefits to DOE

Work conducted in FY 2015 has made progress toward an enhanced dynamic modeling capability for integrated energy systems that could play a major role in future U.S. energy planning and development. This capability will aid the nation as it seeks to reduce environmental impacts through incorporation of low-carbon thermal and electric energy sources, such as nuclear and renewable technologies. Data necessary for preliminary validation of the nuclear subsystem model has been compiled and will be applied in FY 2016. Models will continue to be enhanced over the next two years of the LDRD scope, incorporating methods developed for evaluating the probability of control-system stability and an advanced, digital alarm system that will, in future hardware-based systems, be able to process real-time input data from sensors located at different energy system components to minimize the potential of component failure. Testing that has been initiated at Ohio State University distributed test facility will provide a basis for future multi-laboratory, integrated testing of simulation models and hardware to further advance NHES concepts. This LDRD project provides INL a mechanism to leverage expertise within the National University Consortium to build an enhanced capability in integrated energy system design and development at INL and its partner universities. These tools and approaches will support the current needs of both DOE-NE and the DOE Office of Energy Efficiency and Renewable Energy, could ultimately impact approaches used within the DOE Office of Electricity, and will enable more rapid adoption of the proposed technology by industry.

Publications

Guo, Q., M. Pietrykowski, C. Liu, and C. Smidts, "A Distributed Test Facility for Cyber-Physical Systems: Part I. Fundamental Principles," *IEEE Transactions on Control of Network Systems*, to be submitted.

Ibekwe, R. T. and C. W. Forsberg, "Firebrick Resistance-Heated Energy Storage: Existing Technology Base," *Transactions of the American Nuclear Society Winter Meeting*, Washington, D.C., November 8–12, 2015.

Guo, Q., *A Distributed Test Facility for Cyber-Physical Systems*, Ph.D. Dissertation, Department of Mechanical and Aerospace Engineering, Ohio State University, Columbus, Ohio, August 2015.

Mikkelson, D., C. Chang, S. M. Cetiner, A. L. Qualls, J. M. Doster, and T. N. Dinh, "Small Modular Reactor Modeling Using Modelica for Nuclear-Renewable Hybrid Energy Systems Applications," *Transactions of the American Nuclear Society Winter Meeting*, Washington, D.C., November 8–12, 2015.

Misenheimer, C. and S. D. Terry, "Modeling Hybrid Nuclear Systems with Chilled-Water Storage," *ASME Journal of Energy Resources and Technology*, to be submitted.

Pietrykowski, M., Q. Guo, and C. Smidts, "A Distributed Test Facility for Cyber-Physical Systems: Part II. Fundamental Verification," *IEEE Transactions on Control of Network Systems*, to be submitted.

Schneider, E. and C. W. Forsberg, "Variable Electricity from Base-Load Nuclear Power Plants Using Stored Heat," *Proceedings of the International Congress on Advanced Nuclear Power Plants*, Nice, France, May 3-6, 2015.

Stack, D. C., "Improving Nuclear System Economics Using Firebrick Resistance-Heated Energy Storage (FIRES), *Transactions of the American Nuclear Society Annual Meeting*, San Antonio, Texas, June 7-11, 2015.

Stack, D. C., "Impact of Firebrick Resistance-Heated Energy Storage (FIRES) on Electricity Prices in a Nuclear Renewable Grid," *Transactions of the American Nuclear Society Winter Meeting*, Washington, D.C., November 8-12, 2015.

Presentations

Guo, Q., M. Pietrykowski, and C. Smidts, "Dynamic Data Transmission Frequency Decision for Distributed Control Systems," NPIC-HMIT 2015, Charlotte, North Carolina, February 23–26, 2015.

Teeter, L., F. Teng, W. Marcum, J. Kruzic, M. Anderson, and J. Tucker, "Supercritical Carbon Dioxide System for Materials Corrosion Testing," Minerals, Metals & Materials Society Annual Meeting, Orlando, Florida, March 2015.

Patents

Smidts, C., Q. Guo, and M. Pietrykowski, Distributed Test Facility for Digital Instrumentation and Control Systems, patent application to be submitted 2015.

15-040—Acoustic Telemetry Infrastructure for In-Pile ATR and TREAT Monitoring

Vivek Agarwal, James A. Smith, and J. Keith Jewell

Although a nuclear reactor is a hostile environment for sensing and electrical communications, the reactor core is amenable to acoustic communication. It is believed that listening to a reactor's intrinsic and extrinsic acoustic sources using the acoustic telemetry infrastructure will enable an efficient, nonintrusive in-pile measurement of temperature, axial extension, fission gases, neutron flux, and gamma flux when coupled with advanced signal processing algorithms, especially under transient testing. Even early detection of structure failures, pump/vane degradation, and other diverse faults inside reactors is possible with proper sensing and data-processing/classification techniques with no impact on reactor safety or control systems. This research will accommodate sensor-design and signal-processing tools for telemetry systems that use acoustic-based sensors, such as thermoacoustics (TAC) and vibro-acoustics.

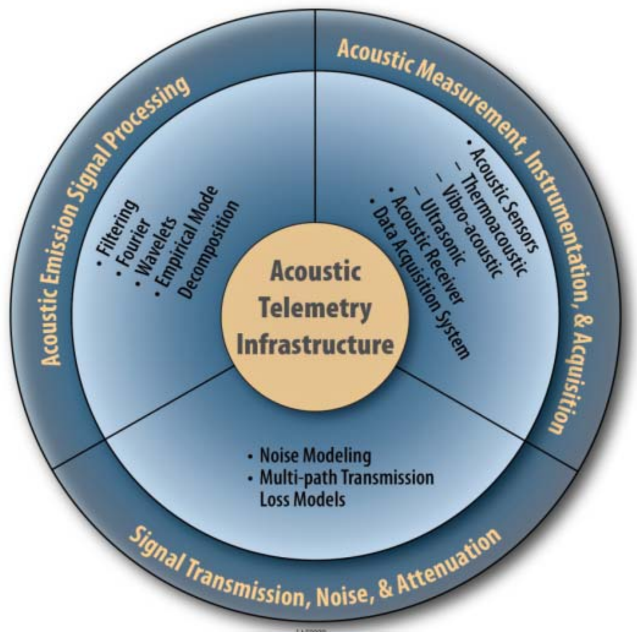

Figure 1. Elements of acoustic telemetry insfrastructure.

The objectives of this research are to develop an acoustic baseline of ATR under different operating conditions, find quiescent frequency regions for sensor operating ranges, develop signal transmission path loss models, and develop customized denoising techniques. This affords the opportunity to obtain the maximum signal-to-noise ratio from the acoustic sensors using the acoustic telemetry infrastructure for ATR and can be adapted for the Transient Reactor Test. The research objectives will be achieved by integrating (a) acoustic measurement, instrumentation and acquisition; (b) signal transmission, noise, and attenuation; and (c) acoustic emission signal processing, as shown in Figure 1.

Summary

The first year of this three-year project focused on developing advanced signal-processing techniques to analyze acoustic signals from eight installed accelerometer sensors in the ATR nozzle trench area. The data analysis characterized changes in signal amplitude, frequency, and phase under different ATR operating conditions. These changes represented reactor states that were validated based on the information in the ATR operation logs. The frequency analysis of the data enabled identification of the quiescent frequency region for TAC sensor development. A senior instrumentation-and-controls scientist and a summer graduate intern were hired to support this research project.

The first-year research outcomes include some key research findings:

- The periodic pressure pulses (fundamental and higher-order frequency harmonics) from the five pump vanes attached to the rotating shaft of the primary coolant pump acted as a virtual TAC signal source. The frequency harmonics generated by the pump vanes (148, 296, and 444 Hz) are postulated to be nearly identical to the signals that will be generated by TAC sensors when inserted into the reactor core. Virtual TAC sensor responses are monitored in real time and processed. This will support development of signal detection and processing techniques prior to the insertion of an actual TAC sensor within the ATR core.

- Figure 2 shows the first acoustic baseline signature (by tracking frequency harmonics of pumps) of the ATR and displays different process states. Observe in Figure 2 that the frequency (spectrogram) signal is responsive to reactor ramping to full power, capturing different stages of ramping (for example, press-up, reactor going critical, power split). Additional reactor states identified include (a) sharp but steady transition to new process state, (b) sharp and unstable transition to new process state, (c) quiescent operation, (d) steady state but bi-stable, and (e) long quiescent operation but noisy state. The amplitude behavior of both spectrogram and fast Fourier transformation highlights the reactor manual scram on July 23, 2015, due to a leak in one of the emergency circulating pumps (shown in Figure 2).
- The first set of virtual TAC signals supports critical findings that (a) ATR noise will not impact TAC operation below 2 KHz, (b) the TAC sensor has high fidelity that will allow for sensitive in-core thermal microstructural and radiation measurements, (c) instabilities by the coolant flow will not interfere with the TAC signal, and (d) multiple coolant inlets and outlets as well as fluid flow in the reactor will not diffuse the acoustic signal from the TAC.

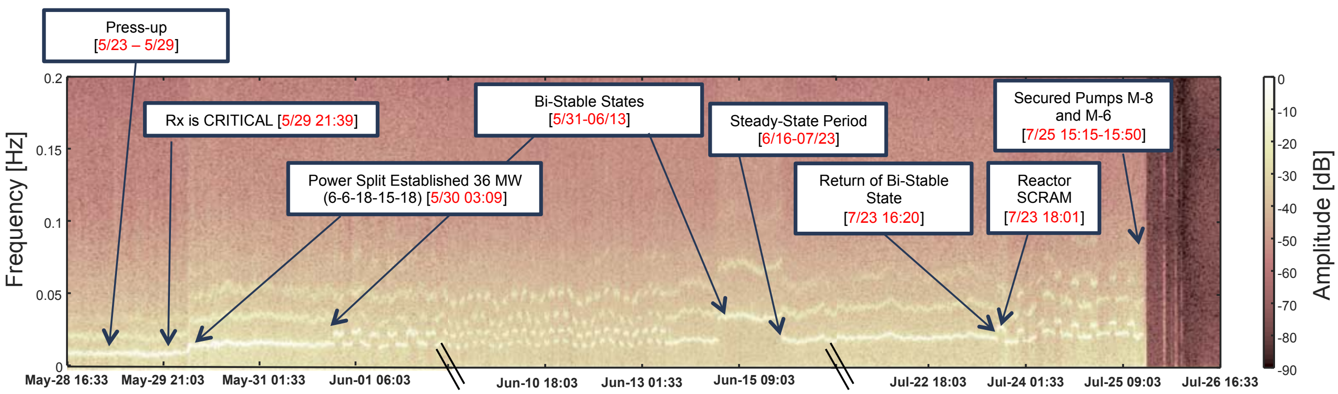

Figure 2. Panoramic view of virtual TAC signals showing different ATR process states from the May 28 to July 26, 2015, period of operation.

Benefits to DOE

This research is critical in advancing DOE's nuclear energy mission by developing an advanced capability of in-pile temperature measurements for materials irradiation in research and test reactors. This research will enable a direct-technology and capability-transfer opportunity to the nuclear industry to support current and next-generation reactor concepts. Successful completion of this research will significantly improve the quality and capability of INL to analyze in-pile data for materials and fuels and to carry out modeling and simulation R&D.

Publications

Agarwal, V., J. A. Smith, and J. K. Jewell, "Monitoring and Analysis of In-Pile Phenomena in Advanced Test Reactor Using Acoustic Telemetry," *Proceedings of the 9th International Conference on Nuclear Plants Instrumentation, Control & Human-Machine Interface Technologies*, pp. 553–561, Charlotte, North Carolina, February 23–26, 2015.

Presentations

Hrisko, J., S. L. Garrett, W. M. Smith, J. A. Smith, and V. Agarwal, "The Vibroacoustic Environment in a Nuclear Reactor," 169th Meeting of Acoustical Society of America, Pittsburgh, Pennsylvania, May 15-22, 2015.

15-060—Development of Efficient TREAT Modeling Capabilities with Graphite Data Improvement

Mark DeHart, Benoit Forget,[1] Kord Smith,[1] and Edward Blandford[2]

This project consists of two independent research tasks being performed by National University Consortium (NUC) teams at the Massachusetts Institute of Technology (MIT) and the University of New Mexico (UNM). Both tasks are in support of different aspects of Transient Reactor Test (TREAT) Facility modeling and simulation. The two primary objectives at MIT are (a) the development of a coupling methodology between the open-source Monte Carlo code OpenMC and the multiphysics framework MOOSE and (b) the implementation of an a priori, thermal-neutron-scattering, cross-section kernel for graphite. UNM is working to perform an experimental study on boiling heat transfer and pressure drop of key accident-tolerant fuel (ATF) clad concepts; these experiments are intended to provide data for validating RELAP-5 and ultimately RELAP-7 boiling heat transfer constitutive model validation requirements and inform TREAT Water Environment Recirculating Loop (TWERL) design.

Summary

FY 2015 was the first year of this project. The work at each of the two universities is being performed in support of TREAT but is not collaborative and is being performed independently. The following subsections describe the work at each university.

MIT

The coupling work between OpenMC and MOOSE is based on an extension of prior work in which Monte Carlo tallies were performed over orthogonal polynomials to facilitate the transfer of power distributions between the constructive solid geometry and finite element mesh. Tallying directly on a finite element mesh used by MOOSE-based software would be computationally and memory prohibitive for any realistic problem. For TREAT, the methodology was extended to the use of Legendre polynomials that are more appropriate for accommodating the Cartesian nature of the reactor. The tally on orthogonal polynomials takes care of the transfer from OpenMC to MOOSE; on the return, MOOSE provides a temperature profile that cannot be readily used in Monte Carlo without fine geometry discretization. This would lead once again to a substantial increase in runtime and storage. To circumvent this problem, continuous material tracking was implemented in OpenMC. This process allows for path length sampling of neutrons in a material with varying properties, in this case temperature.

An OpenMC model of the TREAT reactor has been developed, and testing will begin in Year 2 for the coupled OpenMC/MOOSE simulation.

The first step of the thermal-neutron-scattering work was reproducing LEAPR capabilities for inelastic incoherent scattering, elastic coherent scattering, and elastic incoherent scattering (LEAPR is a module within the widely used a nuclear data processing tool NJOY that is able to calculate thermal scattering cross sections for materials). This process is, for the most part, complete for the inelastic incoherent scattering and well understood for the elastic scattering. Additionally, a new methodology is being envisioned to accelerate the processing using fast Fourier transforms. The goal is to develop a faster processing approach to enable re-computing scattering kernels prior to each calculation at the needed temperature instead of relying on preprocessed data. Faster integration will provide the ability to perform the calculations on the fly and avoid storing tables all together.

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[1] Massachusetts Institute of Technology
[2] University of New Mexico

The advantage of integrating such capabilities in the Monte Carlo simulations is of great relevance to the TREAT reactor, where the graphite-scattering kernels can account for thousands of percent millirho of reactivity if treated improperly and significant fission density spatial errors. These capabilities will allow for greater analysis of the sensitivities of the simulations to different graphite-scattering kernels and lead to improvement in the fidelity of the simulations.

Two Ph.D. students from MIT worked on this project in FY 2015.

UNM

In FY 2015, the project team successfully performed the following tasks: modeled TWERL using RELAP-5, performed a scoping study for void fraction measurement options for TREAT ATF-3 and -4 testing, and initiated surface analysis measurements for SiC and FeCrAl cladding samples

Work activities are under way to develop pool and flow boiling experiment capabilities to provide RELAP-7 constitutive model validation data. Void-fraction, two-phase flow heat transfer coefficient, and critical heat flux (CHF) data will be collected for RELAP-7 boiling heat transfer constitutive models development and validation. Differing from RELAP5-3D, RELAP-7 uses the seven-equation model for two-phase flow with full thermodynamic and mechanical nonequilibrium. One of the unique features of the seven-equation model is reflected in the presence of a volume fraction evaluation. Void fraction will be measured during the convection boiling heat transfer experiment, which will be very helpful for the verification and validation of RELAP-7 two-phase flow constitutive models. Moreover, void-fraction measurement sensors for TWERL and the INL static capsule (SERTTA) are also being developed at the UNM thermal hydraulic laboratory.

Also, as part of this research, CHF data will be collected for RELAP-7 validation studies. UNM has reviewed CHF models of several integral codes, including TRAC, TRACE V5.0, and RELAP5-3D. A CHF look-up table is the default model for all of these codes. The CHF look-up table is based on an extensive database of CHF values obtained in tubes with a vertical upflow of a steam/water mixture. Correction factors are included to improve the accuracy of this table when applied to different flow conditions. CHF data of different types of claddings and flow channels will be collected by the flow boiling experiment (both look-up table and correlations) for RELAP-7.

Because this LDRD is experimentally intensive, a fair amount of effort has been focused on building up these capabilities at UNM. Both the pool-boiling and flow-boiling loop facilities have been essentially completed, and UNM is well positioned to start supporting RELAP-7 validation efforts in FY 2016.

One postdoc and one undergraduate student from UNM worked on this project in FY 2015.

Benefits to DOE

Both projects support different aspects of TREAT modeling and simulation. The work at MIT is intended to improve cross-section generation methods for TREAT in support of INL modeling and simulation efforts, which in turn are being directly supported by the DOE under the Nuclear Engineering Advanced Modeling and Simulation (NEAMS) program. The work at UNM is focused on support for TREAT experiment design and analysis—it supports NEAMS efforts but also supports current experiment design efforts for the ATF program. Thus, both projects support the TREAT mission with the DOE Office of Nuclear Energy. In the longer term, the NEAMS modeling and simulation efforts may potentially support National Nuclear Security Administration efforts for calculations related to conversion of the TREAT Facility to low-enriched uranium fuel.

Publications

Ellis, Matt, Benoit Forget, Kord Smith, and Derek Gaston, "Preliminary coupling of the Monte Carlo Code OpenMC and the Multiphysics Object-Oriented Simulation Environment (MOOSE) for analyzing Doppler feedback in Monte Carlo simulations," *Proceedings of the Joint International Conference on M&C+SNA+MC*, Nashville, Tennessee, April 19–23, 2015.

Presentations

Ellis, Matt, Benoit Forget, Kord Smith, and Derek Gaston, "Continuous Temperature Representation in Coupled OpenMC/MOOSE Simulations," PHYSOR 2016 - Unifying Theory and Experiments in the 21st Century, Sun Valley, Idaho, May 1–5, 2016.

15-071—Determination of Used Fuel Burnup through Fluorimetry of Activation Products

Leigh R. Martin, Aaron Johnson, and Martha Finck

In the production of plutonium, higher burnup fuel may have elements such as americium, curium, and the lanthanides that may be used as markers that, in turn, can be used to estimate plutonium production rates. Developing detection capabilities that are sensitive enough to distinguish even small quantities of these elements is paramount to evaluating whether this comparison is feasible. Fluorescence spectroscopy presents a detection methodology that may be ~1,000 times more sensitive than ultraviolet-visible and infrared spectroscopy that is currently employed for online detection. Although the fluorescence spectroscopy of the lanthanide ions and curium is well established, the same cannot be said for americium due to the facilities and equipment that are required to perform these measurements. The project set out to study the spectroscopic properties of americium fluorescence and to identify whether the luminescence properties can be sensitized such that useful detection limits with a conventional light source could be accomplished.

Summary

The luminescence spectroscopic properties of the 4f elements are well documented in the open literature, and, in principle, all of the 5f elements are also luminescent. The luminescence properties of uranium(IV and VI) and curium(III) are well also documented; however, the same cannot be said for americium. The study of americium luminescence is in its infancy. A thorough search of the open literature identified only 10 manuscripts that report the phenomenon. Furthermore, all of these studies have been performed using the time-resolved laser-induced fluorescence technique, which involves large laser-based systems that would not be very portable for monitoring activities.

The initial research phase of this LDRD was to establish whether or not a conventional light source could be utilized to measure americium fluorescence so that moving away from the large laser-based systems would be possible.

Figure 1 depicts the first americium(III) emission spectra that have been obtained using a conventional xenon lamp as a light source. Further, by using a compact diode laser, researchers on this project were able to determine the luminescence lifetime of the americium(III) aquo ion. This also represents a large step forward in developing a system that could be used in field applications. The lifetime that was measured was in good agreement with the prior literature.

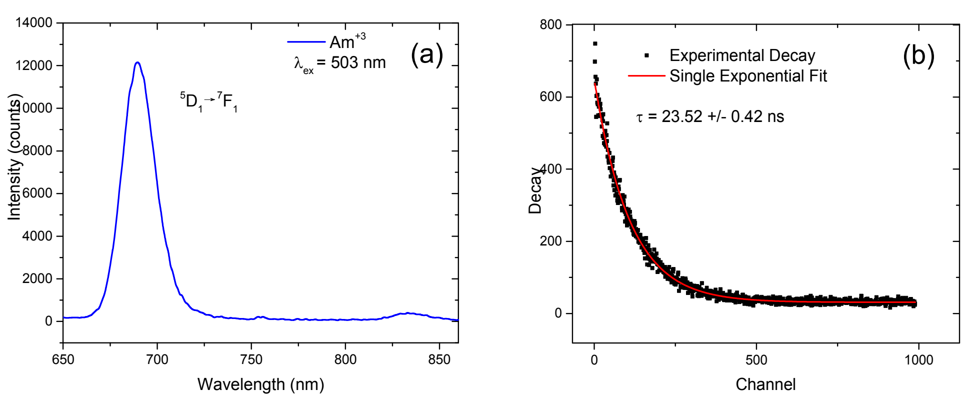

Figure 1. Emission spectra of the $Am^{III}_{(aq)}$ ion, λ_{ex} 503-nm xenon lamp excitation source, 14-nm slit width (a) and fluorescence decay of americium(III), excitation wavelength: 508-nm diode laser. $[Am^{III}] = 9 \times 10^{-3}$ M, $[HClO_4] = 0.3$ M (b).

Because the electronic *f-f* transitions that result in fluorescence spectral properties for the actinide and lanthanide elements are Laporte forbidden, the resulting absorption or emission spectra are very weak in nature. Researchers have investigated different techniques to enhance the resultant spectra. The use of sensitizing chromophores has been shown to enhance the emission from these weakly emitting ions, allowing for ultra-sensitive analysis.

Researchers on this project looked to the use of β-diketone complexes of americium to accomplish americium sensitization. Figure 2 shows the americium emission spectra when complexed to the β-diketone 1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (FOD) and phenanthroline.

The americium FOD/phen complex has a large absorption band in the ultraviolet region that allows for very strong absorption through which large amounts of energy can be deposited into the ligand. This energy is then subsequently deposited into the 5f6 electronic energy levels of the americium(III) ion via an intramolecular energy transfer mechanism. It can be seen from Figure 2 that the resultant emission spectra, when americium is excited through the ligand in this manner, results in at least a doubling of the emission intensity. It is believed that this is the first evidence of americium-sensitized emission spectra to be reported. Further research is required to determine the exact energy transfer mechanism for americium and also to identify whether there are more efficient ligand systems that would be useful to expand this phenomenon further.

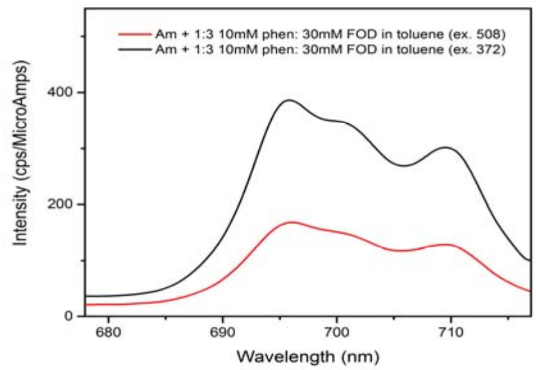

Figure 2. Complexed americium(III) emission spectra, - λ_{ex} 508-nm laser diode, - λ_{ex} 372-nm conventional xenon lamp.

Benefits to DOE

Developing novel techniques for the online monitoring of process raffinates could yield an indirect methodology that can track used fuel burnup. This technology could potentially be used to track mass balance in peaceful fuel reprocessing activities or to identify proliferant operations. The results generated here would also provide a novel contribution to both the actinide and lanthanide coordination chemistry and separations literature.

15-082—Advanced Fission-Chain and Multiplicity Analysis

Matthew T. Kinlaw

This project focused on advancing the current understanding of fission-chain initiation and propagation within multiplying assemblies, with the goal of extending the associated analytical framework to provide enhanced accuracy and minimization of assumptions. Within the standard analytical framework (e.g., coincidence counting and multiplicity analysis based on a point-kinetics framework), extensions to the existing theory are needed to address the initiation of fission chains by an external source. Furthermore, additional information may be available from typical neutron multiplicity distributions, which can be leveraged to better inform corresponding analyses. As an example, if a fissile assembly's inherent neutron die-away can be separated from that of the detection system, the characteristics of that die-away can be exploited to more accurately select the parameters (e.g., neutron number distributions) to be used in subsequent analyses. This is especially important for applications where the assembly and/or surrounding matrix are unknown.

Summary

With the current analysis methodology, extracting the multiplication value of an inspected assembly requires known neutron number distributions. The choice of the specific number distribution to be used is highly dependent on the source that initiates the fission chains and the presence of material near the assembly. In many cases, the source neutrons' origin may be known a priori or can be more easily identified through basic deduction. However, the correct choice of induced-fission neutron number distributions may be challenging to predict, especially when reflector materials surround, or are located within, the multiplying assembly. As an example, consider a bare assembly composed of highly enriched uranium, where the fission chains are induced with a Cf-252 source. In this case, the $\nu_{s,n}$'s are calculated from the spontaneous fission neutron number distribution for Cf-252. The more precise value of M is found when using ν_n's calculated from 2-MeV induced-fission neutron numbers for U-235. However, measurements have shown that the presence of sufficient amounts of reflector material surrounding the assembly greatly affects the choice of ν_n's. In the case of INL's MARVEL (formerly the Argonne Fast Source Reactor core), multiplicity measurements collected with the MARVEL item surrounded by 15 cm of polyethylene suggested the dominant process was single-neutron-induced fission (all $\nu_{s,n}$'s=0), with 1-MeV induced-fission of U-235.

Previous multiplicity analysis of pulsed linac data has generated some interesting conclusions in this area with plutonium-bearing inspection objects. In contrast to the case where fission chains are initiated by spontaneous fission events or relatively small-yield neutron sources (e.g., americium-lithium source), the number of neutrons produced during the linac pulse result in accidental coincidence events that largely compose the total. Analysis is then performed by assuming fission chains are initiated by delayed neutrons that are emitted between linac pulses. With the linac-based data, it was observed that, when analyzing the delayed neutron regions, the more precise values of the assembly multiplication were calculated by assuming that the spontaneous fission of Pu-240 actually drove the fission chains in the delayed neutron region. It may be concluded that the external source is of little benefit when sufficient Pu-240 (or an alternative spontaneous fission source) is present in the multiplying assembly. For an item of similar composition to MARVEL, which contains only enriched uranium, an external source is necessary to initiate a sufficient number of fission chains for statistically reliable analyses. For this case, the current effort investigated the effects of an external neutron generator relative to the optimal fission-chain initiation rate inside a defined assembly. Optimal rates for this investigation were defined as the fission-chain initiation rates at which the relative uncertainties associated with the doubles and/or triples moments were minimized.

Benefits to DOE

Neutron multiplicity measurements continue to be utilized for characterizing fissile material in nuclear accountancy applications, as well as for detecting and identifying assemblies of nuclear material for nonproliferation and international security applications. Significant advancements to the theory and analytical framework of this area have direct application to the detection and characterization of nuclear materials and proliferation signatures and can contribute to the training of emergency responders to nuclear and radiological threats.

15-094—Evaluation and Demonstration of the Integration of Safeguards, Safety, and Security by Design (3SBD)

Jay Disser, Edward Blandford,[1] Edward Arthur,[1] and Bobbi Merryman[1]

The objective of the Safety, Security, and Safeguards (3S) by Design (3SBD) concept is to capture, and potentially optimize, the 3S interrelationships present at nuclear facilities. Although 3SBD has been discussed at many levels since 2008, research has been insufficient to prove that 3SBD can be used as an approach to quantify 3S rather than just being a high-level concept. This LDRD intends to show quantitatively the interrelationships among 3S (including cybersecurity) by focusing on a pebble-bed, fluoride-salt-cooled, high-temperature reactor (PB-FHR) concept. This LDRD also intends to provide nuclear reactor operators and designers with a cost-effective method to integrate 3S considerations into reactor design and provide a risk-informed decision-making platform for 3S personnel. Because the PB-FHR design process is in its beginning stages, the system was chosen as a test case for a quantitative application of the 3SBD approach. Insights resulting from the analysis are expected to be relevant to other advanced reactor designs, namely the gas-cooled, pebble-modular reactor and potentially low-pressure coolant reactor designs such as the sodium-cooled fast reactor.

The PB-FHR concept is being developed through a collaboration that includes the University of California-Berkeley, Oak Ridge National Laboratory, and the Massachusetts Institute of Technology. Pebble-bed reactors such as the PB-FHR are different from traditional reactors, such as light-water reactors, because the fuel consists of large numbers of fuel pebbles that flow through the reactor core. The PB-FHR could have as many as 644,000-cm^3 fuel pebbles in the core with 10,800 of these pebbles circulating through the core every day.[2]

Summary

The technical approach for this project is to:

- Use RELAP5-3D to create a series of pertinent accident and security scenarios and to model the physics of the reactor under these conditions
- Use RAVEN to create a dynamic event tree of the perturbations of different parameters from RELAP5-3D and SAPHIRE and to develop risk limits for those parameters with respect to core damage
- Model a stack of different scenarios, and develop the limit surface of temperature-to-core failure in order to fully understand all of the strengths and weaknesses of the PB-FHR reactor.

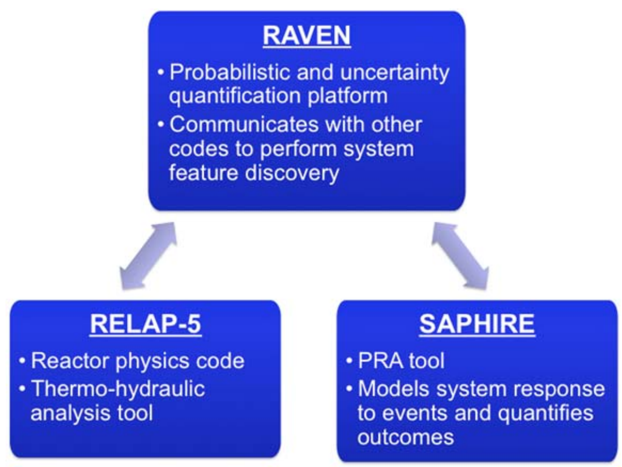

Figure 1. 3SBD computational framework.

The RELAP-53D is a reactor physics code to complete the thermohydraulic analysis of the PB-FHR. SAPHIRE is a probabilistic risk assessment tool and will be used for the international safeguards portion of the project. Both of these programs will be coupled by the RAVEN program, which will perform the probabilistic and uncertainty quantification (Figure 1).

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[1] University of New Mexico

[2] Andreades, Charalampos (Harry), et al., *Technical Description of the "Mark 1" Pebble-Bed Fluoride Salt Cooled High Temperature Reactor (PB-FHR) Power Plant*, UCBTH-14-002, University of California-Berkeley Department of Nuclear Engineering Report, 2014.

Thus far, the PB-FHR has been modeled in RELAP, and the operating scenarios that will be evaluated have been decided upon. Over the summer of 2015, an undergraduate intern from the University of New Mexico worked on integrating RELAP with RAVEN. The student also programmed into RAVEN the sampling methodology that will be used in the dynamic event tree analysis. A preliminary assessment of the PB-FHR concept with regard to international safeguards was also completed. This assessment outlines the different safeguards approaches to the PB-FHR, possible diversion scenarios, and ways to strengthen safeguards at this reactor. This assessment will be used as the foundation for the safeguards portion of the project in Year 2.

Benefits to DOE

This project will place the United States in a stronger position when engaging other countries on 3SBD for critical nuclear infrastructure by providing a more objective method for 3SBD evaluation. This project will also establish the foundation to move 3SBD from a concept to practice. China is actively developing and demonstrating two-pebble bed reactors. The Chinese PB-FHR is being developed by the Chinese Academy of Sciences and is expected to start construction in 2017. Because a cooperative research and development agreement between the Chinese Academy of Science and Oak Ridge National Laboratory has been signed, there could be an opportunity to support this ongoing work with research focused on safeguards and security considerations.

15-141—Interfacing MOOSE Components to Enhance Capability

Hongbin Zhang, Carol Smidts,[1] Xiaodong Sun,[1] and Jinsuo Zhang[1]

The purpose of this LDRD is to expand the capabilities of MOOSE components with respect to hardware-in-the-loop (HIL) testing and testing of digital instrumentation and control systems, modeling of release of fission products, and modeling of material corrosion and thermal hydraulics.

In the area of release of fission products and materials corrosion, the available data have been summarized, the assessment of the project from an experimental point of view started in May 2015, and an experiment plan has been developed to determine the hydrolysis behavior of selected fission products from simulated fuel pellets. Methods to synthesize (press and sinter) simulated fuel pellets of varying composition have been identified and will be developed with an OXY-GON furnace system. Fission-product release experiments for high-temperature water coolant will be conducted in a high-temperature loop that can simulate the operation conditions of a light-water reactor (LWR). The leaching/hydrolysis rates measured will be evaluated using the BISON/MOOSE model. In addition to the coolant water, the project is investigating the dissolution of fission products into liquid sodium for advanced reactors. This will enhance the MOOSE/BISON capabilities for studying metallic fuel/liquid metal systems.

In the area of thermal hydraulics, the objective of the task is to support the two-phase flow modeling and validation activities by investigating the thermal nonequilibrium, five-equation, drift-flux model (DFM). The development of this model can relax the thermal-equilibrium assumption in the classic four-equation DFM when it is applied to model thermal nonequilibrium phenomena encountered in LWRs. Work is being performed to review and improve the closure relations for the five-equation DFM model.

In the area of the distributed test facility, the project objectives are to investigate the connection between RAVEN/RELAP-7 and the distributed test facility (DTF) for instrumentation and control systems. A reduced-scale, HIL steam generator water level control system (which has previously been built at Ohio State University [OSU]) and a full-scale Nuclear Power Plant Simulator will be used to interact with RAVEN. This will allow capabilities to be extended in the area of instrumentation and control validation and verification and HIL testing.

Summary

Release of Fission Products and Materials Corrosion

The assessment of the project from an experimental point of view started in May 2015. An experiment plan has been developed for determining the hydrolysis behavior of selected fission products from simulated fuel pellets. The aim was to determine the time-dependent change of the speciation of fission products leaving the fuel and interacting with the coolant (high-temperature/pressurized water). For the interaction of fission products with boric acid (pressurized-water reactor conditions), it was concluded that with the project's current equipment, measurements can be conducted under post-loss-of-coolant-accident temperatures and normal operating temperatures. In addition to the coolant water, the project team is investigating the dissolution of fission products into liquid sodium for an advanced reactor. This will enhance the MOOSE/BISON capabilities for studying metallic-fuel/liquid-metal systems. During 2015, the laboratory was being set up with equipment for high-temperature work under inert conditions. For this purpose, argon-evacuated gloveboxes were installed in June/July 2015, and suitable small-scale furnaces were purchased that allow various studies to be performed, e.g., liquid sodium-fission product interactions in the near future. The volatility and speciation of some fission products are known to be different in liquid sodium than in LWRs and are planned to be compared for selected elements. In particular, volatile iodine species and hygroscopic iodine aerosols will be less volatile and more

[1] Ohio State University

stable in a sodium-cooled reactor and can therefore lead to the formation of further metal iodides. A main focus of the initial investigations is the determination of the solubility of rare earth elements (e.g., lanthanum, cerium, and gadolinium) in molten sodium independent of the presence of impurities (e.g., oxygen, chloride, and hydrogen). The sodium-related research is currently supported by a Nuclear Energy University Program project collaboration with INL and Los Alamos National Laboratory.

Thermal Hydraulics

The five-equation DFM was developed based on the four-equation DFM formulation. The classic four-equation DFM treats the two-phase flow as a mixture to establish the mass, momentum, and energy balance equations. An additional energy balance equation for the dispersed phase is introduced, which can relax the thermal-equilibrium assumption with proper manipulation in the equation. Based on this additional conservation equation, the temperature of the dispersed phase can be assumed to be the saturation temperature, which can represent most of the thermal nonequilibrium scenarios that may occur in LWRs, including subcooled boiling and post-dryout vapor superheating. A literature survey of the constitutive models (closure relations) has been conducted to review appropriate models available for the dispersed-phase mass-generation rate, interfacial energy transfer, distribution parameter, and drift flux velocity correlations, etc. Constitutive models that have been applied to multiple system analysis codes, such as RELAP5, are reviewed and selected for the five-equation DFM with proper improvement. For instance, some of the representative correlations for the distribution parameter and drift flux velocity have been reviewed to examine their applicability to thermal nonequilibrium scenarios.

Distributed Test Facility

OSU is in the process of obtaining a license for RAVEN. Because RAVEN has never been licensed, this process has included the creation of a license on the INL side, as well as institutional negotiations between OSU and INL involving the license terms. This project team has supported this transaction.

The connection of RAVEN to the DTF requires the inclusion of failure modes for hardware components in the HIL system and the ability to trigger these modes with RAVEN. First, the project team considered the failure modes of a valve in the turbine bypass system. The failure-modes-and-effects-analysis method was used to analyze the performance of the turbine bypass valve. The operational modes for the turbine bypass valve are defined as plugging, internal leakage, internal rupture, external leakage/rupture, and spurious operation. Equivalent behavior methods are being used to study the effect of the real failure modes and their influence on the system's performance. The equivalent failure modes are being implemented in the HIL setup described above. RAVEN will be able to set the status of a valve in the HIL system to one of these modes. This will be the first use of RAVEN within an HIL system.

A full-scale nuclear power plant simulator has been considered for integration with RAVEN and/or the DTF. First, the simulator source code was obtained and examined to find the appropriate variables that need to be replaced by values from the HIL system. The simulator was configured so that system variables can be accessed and modified by external codes. This required modifying and recompiling the simulator source code. The full ramifications of these changes are still being investigated. The appropriate variables are then transmitted to the hardware, creating an HIL setup that includes the simulator. This configuration also allows RAVEN to interface with the simulator directly. RAVEN would be able to invoke the simulator, the HIL system, or both. Because the simulator models a full-scale system, the variables need to be appropriately scaled before being implemented by the hardware. Issues with this specific scaling case have been investigated, and, in general, the solution to this scaling issue will be incorporated into DTF components to ease the use of mixed-scale components.

Benefits to DOE

Release of Fission Products and Materials Corrosion

The interactions (release rates, solubility, and diffusion coefficient) between fission products and primary coolants (water and liquid sodium) obtained can be incorporated into MOOSE/BISON to enhance MOOSE capabilities for coolant-fuel interaction. In addition, a system-level corrosion/precipitation model, which is currently available for liquid-metal loops, will be extended to study the fission products transport in liquid sodium and liquid water and to study the effects of fission products on materials corrosion in FY 2016. This model can be incorporated into BISON or RELAP.

Thermal Hydraulics

The development of the thermal nonequilibrium drift-flux model will help address the modeling challenges for the conventional DFM when treating thermal nonequilibrium phenomena frequently encountered in LWRs but will reduce the computational and model difficulties associated with the detailed two-fluid model. The five-equation DFM can be implemented into a computer code to be developed based on the MOOSE framework and validated against available experimental data.

Distributed Test Facility

The connection of RAVEN to the HIL setup at OSU will be the first use of RAVEN in conjunction with physical components, thereby extending RAVEN's capabilities. The connection of RAVEN to the full-scale nuclear power plant simulator will similarly extend RAVEN's capabilities to interface with other complex software.

Presentations

Zhang, J. and S. Tietze, "Extend MOOSE Capabilities in the Area of Corrosion, Chemical Interactions and Accidents," Idaho National Laboratory – National University Consortium Collaboration Projects Annual Review Meeting, Idaho Falls, Idaho, July 28–29, 2015.

Zhang, X. and X. Sun, "Interfacing MOOSE Components to Enhance Capability: Thermal Non-equilibrium Drift-flux Model and its Implementation into RELAP-7," Idaho National Laboratory – National University Consortium Collaboration Projects Annual Review Meeting, Idaho Falls, Idaho, July 28–29, 2015.

15-142—New In-Core Neutron Diagnostics at the University of New Mexico

Maria A. Okuniewski

The objective of this research is to develop and characterize a new technology for neutron dosimetry that opens a new range of detector materials and applications. Neutrons create defects in and therefore damage materials. This damage includes lattice displacements. As has been shown previously, optical materials may be examined directly for these defects through changes in the refractive index. This project has developed a high-precision method for determining the change in the refractive index in crystals, which the project team successfully demonstrated with neutron-irradiated crystals. High-resolution characterization is being pursued to correlate neutron fluence to radiation damage and index change.

Summary

This technology has many benefits, which may be expanded further with future research. Crystals can be chosen for extremely harsh environments, and this technology may have applications to neutron dosimetry for pyroprocessing or within reactors. Activation foils/wires typically depend on activation and radioactive decay; however, this technique can serve as a complementary neutron measurement of different properties that are not subject to decay (e.g., optical properties). This could find follow-on funding in industry for neutron dosimetry in reactors and fuels-processing applications.

The project team also plans to develop and characterize live-time monitoring. Because the refractive index correlates with the integrated dose, the difference in readings over time gives an active dose rate. Frequency readings of ~100 milliseconds can be used. The readout process is based on the high-frequency (~10 GHz) to low-frequency (~100 MHz) resonance ratio, allowing for high-resolution readings with even <1-millisecond frequency samples.

As a further benefit, follow-on work could pursue remote readouts, which could have possible applications to time-dependent neutron field characterization for the Transient Reactor Test Facility, as well as the light-water fleet and research reactors.

The technique examines the ratio of resonance frequencies for the crystal and the optical cavity and is shown in schematic form for a laser cavity in Figure 1; fiber-optic coupling for standoff, live-time measurements are part of the current research.

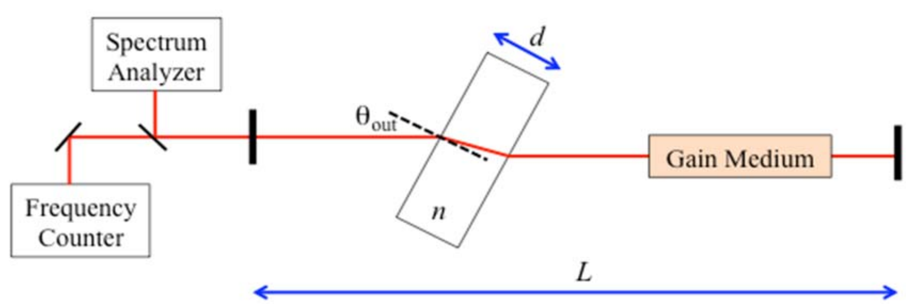

Figure 1. Schematic of laser cavity of length L with sample crystal inserted as a Fabry-Perot etalon at angle theta to the laser cavity light path.

The project is collaborative between INL and the University of New Mexico (UNM), and work in nuclear engineering at UNM is in collaboration with optics work in physics. The research involves several graduate students. This innovative technique opens a new range of materials for neutron dosimetry, and future work will benefit from the properties of the different materials such as corrosion or acid resistance. The growth potential is enormous.

The funding for FY 2015 only became available July 2015, leaving less than a three-month period for the work before the end of September 2015 (end of the fiscal year). The proposed tasks for this short period were:

- Acquisition and testing of a fast photodiode assembly and high-frequency spectrum analyzer
- Examination of unirradiated and previously irradiated crystal samples for comparison with prior measurements on the prior hardware
- Submission of an annual report for Year 1.

The project has received the equipment and new crystal samples to irradiate (Figure 2). The project team is setting up the equipment to test and will examine the previous samples, both irradiated and unirradiated, to confirm sensitivity. One piece of equipment has been delayed; a high-speed photodiode (>30 MHz response) was in stock with the company Albis Optoelectronics when ordered, but the equipment was sold to someone else while the team's order was being processed. A new photodiode will be made but not before the end of the fiscal year, so examination of the index of crystal samples will begin FY 2016.

Figure 2. CaF_2 crystals for neutron damage index of refraction measurements.

A new graduate student started with the project on August 1, 2015, and is anxious to get started with measurements and with simulations. Because simulations do not require the equipment, the student has started learning simulation coding. She has learned how to program and run simple atomistic and molecular-level simulations to understand and simulate crystal damage. The student has also studied mode locking to better understand and utilize the laser setup in the future, and she has studied color centers to understand atom displacement and how it affects optical properties of irradiated materials.

The project team has started with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) molecular dynamics code to understand and predict radiation damage in the optical crystals, and students attended Los Alamos National Laboratory run workshops on LAMMPS (see http://lammps.sandia.gov/workshops.html for details) at UNM August 5–7, 2015. Another faculty member is working with LAMMPS for reactor materials damage simulations, and meetings are being set up to aid the project team in learning the code.

Benefits to DOE

Measurement and characterization of neutron fields are important for INL. The work adds new technology and range of materials to the instrumentation available for characterizing radiation fields. This technology could play into validations for theory and calculations on radiation materials damage because it allows nondestructive assessment of structural changes in material. Nondestructive analysis will provide options to further irradiate the same system, to examine bulk effects, etc.

15-143—Development of Bayesian Uncertainty Quantification Tools for Use in Complex Modeling and Simulation Code Validation

Douglas Burns

The purpose of this research is to develop methods for uncertainty quantification of complex calculations such as those included in modern computer codes used for engineering and safety applications. The methods analyzed in the research are based on the statistical theory presented by Kennedy and O'Hagan.[1] The methodology combines Bayesian statistical analysis techniques with likelihood methodologies, using a Gaussian process assumption for the distribution of unknown calibration parameters to produce a procedure for uncertainty quantification of model predictions.

The uncertainty quantification methodology is being tested on models used to predict seismic ground motion. These models were developed in support of the Pacific Earthquake Engineering Research Center Next Generation Attenuation modeling program known as NGA-West 2.[2]

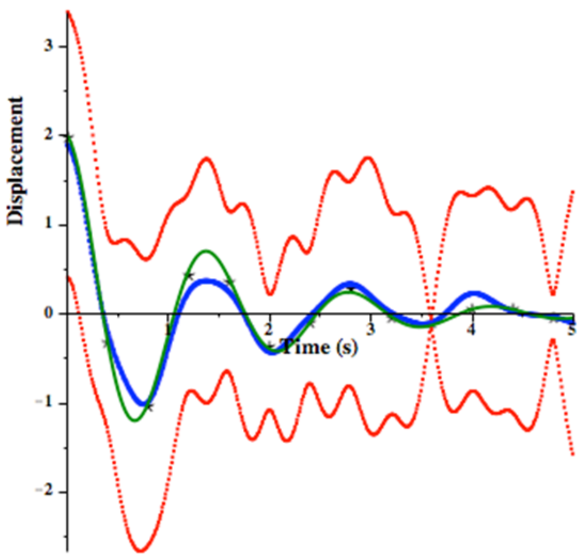

Figure 1. Spring model uncertainty quantification example. The model's analytical output is shown in green, the 13 data points used to train the prediction algorithm are shown by stars, the predicted mean model output based on the 13 training points is shown in blue, and the calculated +/- 2σ prediction uncertainty bands are shown in red. Note that calculated uncertainty collapses to near zero when the predicted model output matches a training data point value.

Summary

The methodology evaluated in this research concentrates on quantifying uncertainty associated with inputs to complex computer codes and on an analysis of how that uncertainty affects outputs of the code. The uncertainty quantification mathematics discussed by Kennedy and O'Hagan has been explored, and software that implements the mathematics on a simple spring model that includes three uncertain calibration parameters has been completed. Figure 1 shows an example of the spring model results using 13 synthetic measurement design points. A sensitivity study of how the uncertainty quantification process responds to changes in the number of training data points has been performed.

The AS08 ground-motion prediction equation in Abrahamson et al. (2014)[3] is being evaluated using the uncertainty quantification methodology. The model is one of five empirical ground-motion prediction tools that have been developed as part of the NGA West 2 program for estimation of average horizontal ground accelerations produced by shallow-crustal earthquakes. The Abrahamson model is applicable to earthquakes of Magnitude 3.0 to 8.5 at distances of 0 to 300 km and spectral periods of 0 to 10 seconds.

[1] M. C. Kennedy and A. O'Hagan, "Bayesian Calibration of Computer Models," *Journal of the Royal Statistical Society B*, Vol. 63, Part B, pp. 425–464, 2001.

[2] Pacific Earthquake Engineering Research Center, *Enhancement of Next Generation Attenuation Relationships for Western US (NGA-West2)*, http://peer.berkeley.edu/ngawest2/, web page visited December 15, 2015.

[3] N. A. Abrahamson, W. J. Silva, and R. Kamai, *Update of the AS08 Ground-Motion Prediction Equations Based on the NGA-West2 Data Set*, PEER Report 2013/04, Pacific Earthquake Engineering Research Center, May 2013.

Seventeen ground-motion records collected at INL's ATR site have been gathered for use in training the uncertainty quantification analysis. The records show peak ground acceleration at the ATR site for seismic events of Magnitude 3.3 to 5.0 and distances of 138 to 214 km that occurred between October 2013 and January 2015.

As part of the LDRD to date, the Abrahamson model has been converted into the R programming language, an interface between the R script and Dakota Version 6.2 has been developed, and several hundred parameter sensitivity and model calibration runs have been completed using Dakota as the analysis driver. The parameter sensitivity analysis indicates that the Abrahamson model output results are insensitive to all but three of the model's input parameters given southeastern Idaho geologic conditions. The ongoing calibration analysis indicates that the Abrahamson model generally under-predicts ground acceleration measured at the ATR site, but further analysis is needed to identify possible causes for the under-prediction. Further work is also planned to develop results similar to those shown in Figure 1 for the Abrahamson model and to perform uncertainty quantification analyses for the other four NGA West 2 ground-motion prediction models.

Benefits to DOE

This research is developing mathematics that could be incorporated into analysis tools such as the RAVEN code being developed at INL. The research is also quantifying uncertainty associated with ground-motion models that could be used to help analyze seismic risks for U.S. nuclear reactors.

15-144—Investigation of Sonication-Assisted Electrolytic Reduction of Used Oxide Fuel in Molten Salt

Shelly Li and Haiyan Zhao[1]

Electrolytic reduction is an integral step in pyroprocessing to treat used fuel from light-water reactors (LWRs) and other metal oxides. The limiting step in electrolytic metal-oxide reduction is slow oxygen-ion diffusion through the used fuel particulates inside the cathode basket. This limiting step leads to low current efficiency, long operating hours, and re-oxidation of reduced metal fuels. Extensive R&D activities have been conducted in the past decade to improve the oxygen-diffusion process associated with the electrolytic reduction of used LWR fuel in high-temperature molten salts. Sonication is a mature technology to improve a variety of chemical/physical processes, including chemical reactions and mass transports. But sonication technology has not been explored to improve the electrolytic-reduction process. This LDRD project provides a great opportunity to investigate the feasibility of improving electrolytic reduction of used oxide fuel in molten salts using the ultrasound technique.

Summary

In this project, sonication apparatus will be applied to an electrochemical cell with molten LiCl-Li_2O at 650°C. The effect of sonication for improving the performance of electrolytic reduction of surrogate metal oxide, such as TiO_2 or MnO_2, will be studied at the Center for Advanced Energy Studies (CAES) at the University of Idaho (UI). Then the sonication-assisted electrolytic reduction of depleted UO_2 will be investigated at both UI/CAES and the INL's Fuel and Applied Science Building.

Funding for this LDRD was not available until June 10, 2015. During the last three months of FY 2015, the work focused on preparations and training to establish the metal-oxide reduction capacity at CAES. A graduate student, Eric Song, has been recruited and began to work on the project. The experiment plan for metal-oxide reduction in high-temperature molten with sonication has been laid out. An aqueous system using a potentiostat has been established at a CAES analytical chemistry laboratory for training purposes. Dr. Haiyan Zhao and Eric Song have obtained hands-on experience on a number of electrochemical measurement techniques by working with the system. This experience is crucial for performing forthcoming electrolytic-reduction tests in high-temperature molten salts. UI has worked with a vender to design and purchase a customized ultrasonic horn/probe that is suitable for the laboratory-scale, electrolytic-reduction system at the elevated temperature.

Meanwhile, experimental design, materials procurement, and equipment preparations are complete (Figure 1). The electrode bundle will include (a) thermocouples, (b) a reference electrode, (c) a cathode with fuel basket, (d) a supporting column, and (e) the sonicator probes, as shown in the figure. The electrolytic reduction of metal oxides with sonication is ready to be carried out at the CAES Radiochemistry Laboratory in FY 2016.

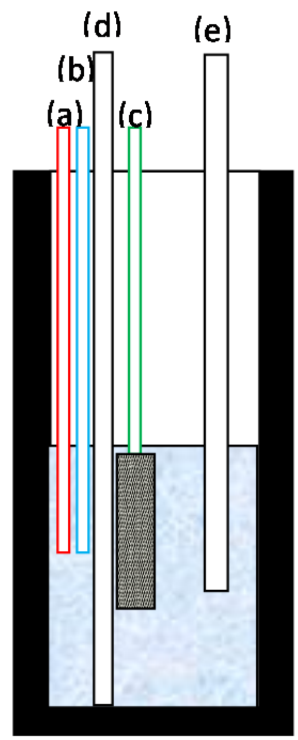

Figure 1. Experimental setup for electrolytic reduction.

Benefits to DOE

The agitation through sonication will be expected to accelerate oxygen-ion diffusion, improve the contact between the fuel particulate with the cathode, and drive the trapped O_2 molecules diffusing out of the packed fuel bed in the adhesive molten salt. If the proposed research proceeds as expected, it will successfully resolve one of the key

[1] University of Idaho

needs associated with scale-up pyroprocessing. The research will expand expertise in the electrolytic reduction of used LWR fuels for pyroprocessing and further establish INL as a world leader in innovative fuel-cycle technology. The proposed research is also directly applicable to the projects for recycling rare earth elements under the Critical Material Institute. If this LDRD yields technical advances, funding would be sought through the DOE Fuel Cycle Research and Development Program as well as the Critical Material Institute. The research team will seek to protect intellectual property and publish information in the interest of INL.

15-145—Advanced Neutron and X-Ray Imaging at TREAT

J. Keith Jewell, Robert C. O'Brien, and Tony S. Hill[1]

This LDRD focuses on the development of advanced imaging options for the future Transient Reactor Test (TREAT) experimental program. The aim is to develop a suite of possible imaging capabilities, including x-ray and neutron imagery and radiography, that will extend the scientific and engineering reach of the TREAT experimental program. In the decades since TREAT was designed and instrumented, significant advances have been made in computing, materials, and detection technology and methods. The development work in this LDRD will focus on possible implementations and configurations that improve the spatial and temporal resolution of measurements to the lowest achievable length scales. This work is independent of the TREAT restart and will result in a portfolio of options that leadership can use to broaden the impact of an operating TREAT reactor.

Summary

The project began in mid-summer of FY 2015 and achieved one major accomplishment: conducting the TREAT Advanced Instrumentation Workshop held September 2–3 at the Center for Advanced Energy Studies in Idaho Falls. The workshop was an effort to coordinate the modeling and simulation efforts at INL with the experimental capabilities needed for an extended scientific mission at TREAT. Presentations were given by the multiscale, multiphysics MOOSE development team with a focus on understanding the sensitivity of experiment data and results at lower-length scale modeling. The workshop generated significant discussion on the need for detailed sensitivity studies to determine data liabilities, validation at the lower length scales, and advanced imaging for in situ fuel dynamics.

Benefits to DOE

DOE has decided to reestablish the capability to conduct transient testing of nuclear fuels at the TREAT reactor. Transient testing of nuclear fuels is needed to qualify new high-performance fuels that will improve current nuclear power plant accident tolerance, improve performance and sustainability, and make new-generation reactors more affordable. Transient testing is also an essential process in the development of nuclear fuels that are easier to recycle, safer and more efficient, and more difficult to divert for use in making nuclear weapons. TREAT has been used to study fuel meltdowns, metal-water reactions, thermal interactions between overheated fuel and coolant, and the transient behavior of ceramic and cermet fuels for high-temperature systems. The contributions of TREAT to the reactor safety program can be seen as fourfold:

- To provide basic data for predicting the safety margin of fuel designs and the severity of potential accidents
- To serve as a proving ground for fuel concepts design to reduce or preclude the consequent hazards associated with potential accidents
- To provide nondestructive test data through neutron radiography of fuel samples
- To provide real-time in situ observations of severe accident responses of fuel concepts and the responses of advanced fuels in extreme atmospheric conditions.

Significant transient testing of nuclear fuels has not been conducted in the United States in more than a decade, and very few operating test facilities in the world can accommodate prototype-scale fuel pins. Additionally, most of the operating transient fuel test reactors lack in situ, real-time imaging technology due to access limitations. The TREAT restart program includes re-instantiating existing in situ diagnostic systems, which include uncompensated ion chambers in the radial reflector, thermocouples on a few core assemblies, a

[1] Idaho State University

10-by-36 (360-channel) hodoscope, a fission product detection system (remote sampling), and a pre- and post-irradiation neutron radiography station (asynchronously operated).

The project performs feasibility studies to adapt, develop, and deploy advanced in situ imaging and monitoring technologies and techniques to enhance and expand the capabilities to monitor the movement, location, and performance of fuel, cladding, and other material specimens under test within the TREAT reactor. One example of technology deployment feasibilities that will be examined is the use of microscopy techniques, such as scanning electron microscopy that would otherwise be confined to post-irradiation examination, to examine the real-time microstructural changes in material specimens (such as claddings and new fuels) during exposure to extreme temperature transients. Another example of technologies that will be evaluated is the adaptation of high-energy physics techniques and high-performance x-ray optics to monitor the location, migration, and release of fission products from irradiated fuel specimens.

ENABLING CLEAN ENERGY DEPLOYMENT

13-011—Integrated Approach to Algal Biofuel, Biopower, and Agricultural Waste Management

13-027—Diagnostics of Advanced Energy Storage Materials

13-065—Multi-Domain Modeling, Simulation, and Integration Tools for the Dynamic Analysis and Optimization of Hybrid Energy Systems

13-068—Cooling in Fractured Geothermal Reservoirs: Analyses of Long-Term Cooling in Typical Geothermal Reservoirs and Application to Geothermal Resource Potential

13-079—Diverse Biological Factories for Sustainable Manufacturing

13-110—Nuclear-Renewable-Oil Shale Hybrid Energy System

14-078—Extended Stability Gamma-Gamma Prime Containing Nickel-Base Alloys

14-079—Second-Generation Switchable Polarity Solvent Draw Solutes for Forward Osmosis

14-080—Battery Material Characterization Technologies

14-086—Development of a Microgrid/Smart Grid Test Bed for ESL and Super Lab Initiative, with Load Variability Characterization and Control for Renewable Energy Integration

14-091—Battery Health Estimation Based on Self-Discharge Fast Measurement and Soft Short-Circuit Detection

14-095—In Situ Measurement of Electrolyte Chemistry in Battery Cells during Operation

14-106—Understanding the Growth of Ultra-Long Carbon Nanotubes

15-125—Phosphoranimines for Advanced Battery Applications

15-128—Microstructural Evolution and Mesoscale-Coupled Flow-Reaction-Fracturing Processes in Organic-Rich Nanoporous Shales

15-135—Dynamic Simulations for Large-Scale Electric Power Networks in a Real-Time Environment Using Multiple RTDS

15-140—Expanding the Utility of Advanced Chemical Physics Models for Electrolytes

15-146—Tailoring the Kinetic Function of a Surface through Electronic Effects of Nanoscale Architecture

15-147—Rare Earth Element Catalysts for Carbon-Based Chemicals

13-011—Integrated Approach to Algal Biofuel, Biopower, and Agricultural Waste Management

Deborah T. Newby, Erik R. Coats,[1] Kevin Feris,[2] Armando McDonald,[1] and Brad Wahlen

More than 9 million dairy cows in the United States generate more than 226 billion kg of wet manure and produce more than 5.8 billion kg of CO_2 equivalents annually. Using a process known as anaerobic digestion (AD), manure such as this can be treated with natural bacteria in the absence of oxygen to produce methane-rich biogas that can be captured and used for the production of electricity or heat. Integrated with AD, residuals (upstream/downstream) can be separated and used for various purposes, including fertilizer, animal bedding, polyhydroxyalkanoates (PHAs, which are biological, biodegradable thermoplastics with significant commercial value), and algae cultivation, as shown in the process flow diagram in Figure 1.

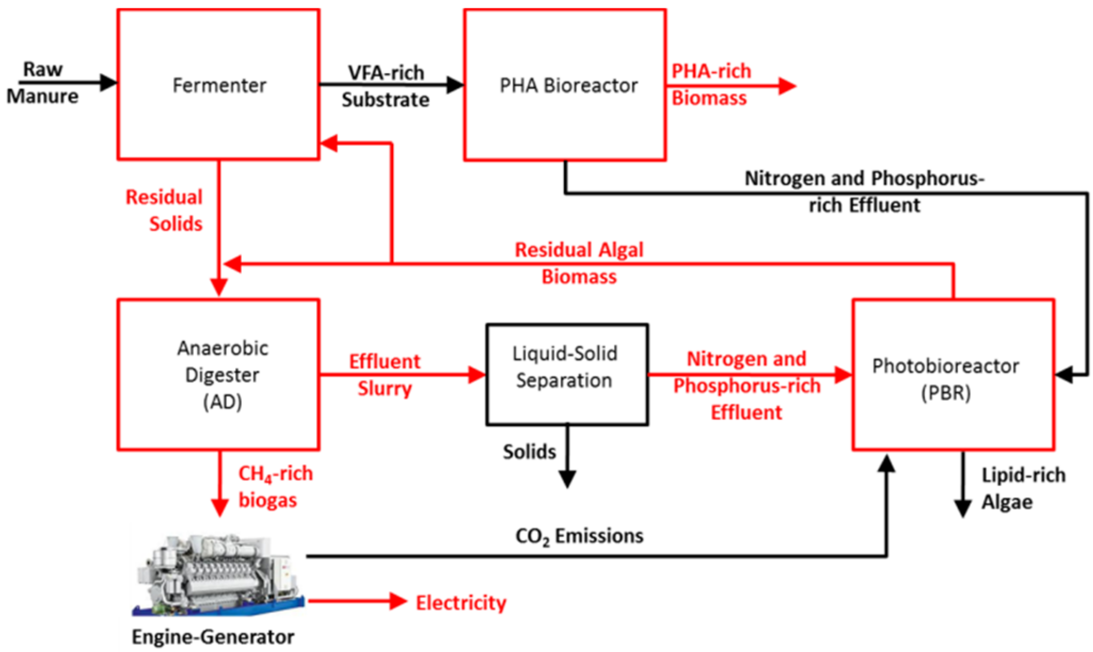

Figure 1. Process flow diagram for the integrated AD-algal operations (nitrogen/phosphorus-rich effluent streams are highlighted in red).

While AD is a mature technology, its growth is stunted due to poor economics and the need to further mitigate the release of emissions (e.g., nitrogen, phosphorus, CO_2) into the environment. However, these nutrients have significant value for large-scale cultivation of algal biomass for biofuels and bioenergy. The goal of this project is to build on and scale up prior work that has established the effectiveness of deploying a novel two-stage AD system coupled with an open algal photobioreactor to produce multiple value-added commodities (biopower, biofuels, PHA, etc.). This research differs from a conventional algal biofuel approach in that it incorporates a strategy to minimize costly nutrient import and reduce water use by connecting algal production to dairy wastewater treatment. Coupling the generation of additional product streams to an established industry that

[1] University of Idaho

[2] Boise State University

demands enhanced waste/emissions management will facilitate enhanced AD algae biofuel adoption by addressing key barriers and enhancing commercial viability.

Summary

Task RO1activities were completed in Year 3 of the project. The goal of these experiments was to characterize the complex of factors in the PHA and AD effluents that influence algal production; optimize annualized algal biomass production yields; determine the economic potential of this biomass as biofuel, bio-oil, and bioplastic feedstocks; and determine operational conditions that minimize water usage and pretreatments that maximize yields. Growth rates and yield of *Chlorella vulgaris* varied by effluent concentration and type. Specifically, the optical properties of the PHA and AD effluents were the primary controlling factor on first-order growth rates of *C. vulgaris*, whereas the total nitrogen content was the primary factor affecting yield. Annualized yields were optimized and water use minimized by blending the two effluent streams in continuous culture and exploring cultivation water reuse. Effluents were blended to maintain optimal optical conditions and total nitrogen concentrations. The findings from this effort suggest that water usage can be reduced by 90% while maintaining high levels of algal biomass productivity. Biomass generated through these experiments has been characterized in terms of lipid and biomass quantity and hydrothermal liquefaction oil yield. Also explored was ultraviolet modification of AD and PHA effluents in continuous culture. Ultraviolet pretreatment maximized algal productivity and carbohydrate content by minimizing the invasion potential of contaminating algal strains.

Task RO2b activities were completed in Year 3, specifically to determine the viability of internally recycling residual algal biomass as a fermenter and/or AD substrate to improve PHA and/or CH_4 production. The research generated a peer-reviewed publication. In brief, a 10% PHA-algae supplement produced 11% more volatile fatty acid (VFA) during fermentation and 11% more methane during anaerobic digestion (vs. dairy manure); the PHA-algae biogas also contained a higher percentage (62.7 vs. 59.1%) of methane than manure biogas. Algal augmentation exhibited no negative effect on fermenter or AD operation. Quantitative real-time PCR showed that the ADs contained substantial populations of both acetoclastic and hydrogenotrophic methanogens, which, given the heterogeneous substrate, enhanced process stability. There were significant differences between PHA-algae batches, and large quantities of chemical oxygen demand were released during algae freezing. It was concluded that PHA-algae yielded more VFA during fermentation and a more methane-rich biogas following AD than dairy manure yielded. A 10% PHA-algae supplement caused no process disturbance in normal manure flora.

One student at Boise State University will defend his thesis and submit a manuscript to at least one publication based on his participation in this project during the fall of 2015. An additional three Boise State University undergraduate students were trained on this project.

Benefits to DOE

This research advances algae technologies by using waste streams as a nutrient source, thereby making broader implementation of commercial-scale algal cultivation for fuels more economically feasible. This research also addresses barriers to wider-scale deployment of AD, which is currently underused due to un-optimized systems and underdeveloped opportunities. New knowledge on a more comprehensive and integrated waste-to-fuels process is needed by the dairy/waste-processing industry to improve the understanding of biological processing of organic matter. Furthermore, this effort provides the basis for strong industrial partnerships by taking this technology from bench scale to the demonstration level. By integrating education and work-force development, skilled bio-product innovators and future system operators have been trained.

Publications

Harper, J., M. Passero, E. R. Coats, A. G. McDonald, D. Newby, B. Wahlen, and K. Feris, “Nitrogen limits yield and optical properties limit growth rate of *C. vulgaris* cultivated in AD effluent,” in preparation.

Harper, J., M. Passero, E. R. Coats, A. G. McDonald, D. Newby, B. Wahlen, and K. Feris, "Optimizing wastewater as a feedstock for algae cultivation: Blending wastewaters as a function of total nitrogen and optical properties maximizes yield and growth rates, " in preparation.

Passero, M., J. Harper, E. R. Coats, A. G. McDonald, D. Newby, B. Wahlen, and K. Feris, "UV-pretreatment of AD effluent in continuous cultivation of *C. vulgaris*: enhancing crop stability," in preparation.

Smith, S. A., E. Hughes, E. R. Coats, C. K. Brinkman, A. G. McDonald, J. Harper, K. Feris, and D. Newby, "Toward sustainable dairy waste utilization: Enhanced VFA and biogas synthesis via upcycling algal biomass cultured on waste effluent," *Journal of Chemical Technology and Biotechnology,* DOI 10.1002/jctb.4706, published online, 2015.

Presentations

Harper, J., E. Coats, D. Newby, and K. Feris, "Mixing AD and PHA Reactor Effluent to Minimize Nutrient Input and Water Consumption of Large-scale Algal Operations," 4th International Conference on Algal Biomass, Biofuels and Bioproducts, San Diego, California, June 7–10, 2015.

Passero, M., K. Feris, R. R. Hillsberry, A. G. McDonald, E. R. Coats, and D. T. Newby, "Pilot Scale Algae Cultivation: UV Pre-Treatment Improves Integrity of *C. vulgaris* in Dairy Wastewater," 4th International Conference on Algal Biomass, Biofuels and Bioproducts, San Diego, California, June 7–10, 2015.

13-027—Diagnostics of Advanced Energy Storage Materials

Eric J. Dufek, Michael V. Glazoff, Lucia M. Petkovic, and Doug Akers

The emergence of new materials for electrochemical energy storage necessitates the development of means to effectively evaluate how different materials interact with each other and how processing techniques impact overall performance. This project is focused on the implementation of multiple optical, spectroscopic, and electrochemical techniques to more fully understand how performance of battery electrodes and systems is impacted as a function of processing and chemistry. Of particular interest to the project is the use of spectroscopic ellipsometry, Fourier transform infrared spectroscopy, imaging techniques such as scanning electron microscopy, other physical characterization methods, and electrochemical performance. The prime materials and interactions of interest to the project are those that occur within the electrolyte, the binder, and with the active materials in the electrodes.

Lithium-ion battery performance is impacted by a multitude of factors, including active materials, electrode configuration, composition, electrode thickness, porosity, and environmental variables. As formulated, composite electrodes for lithium-ion batteries typically are composed of an active material, binder, and conductive additive such as carbon. During processing, cast electrodes can be calendared to different thicknesses, densities, and porosities to influence performance. During cycling, changes in materials such as the formation of the solid electrolyte interphase (SEI) and in expansion-induced fracturing of materials can significantly impact long-term battery performance and can have impacts on secondary degradation mechanisms. It is difficult to fully grasp degradation using a single method; thus, the implementation of multiple methods is necessary to obtain an in-depth analysis. Key objectives of using complementary methods include the ability to follow SEI change during cycling, identify chemical changes that occur with variable binder compositions, follow how mechanical stress and electrode processing impact electrode performance, computationally identify morphological aspects of electrodes, and model how electrode structure can change during cycling. A secondary purpose of the project is to develop methods that show broad applicability to cathode and anode systems, as well as relevancy to emerging battery chemistries.

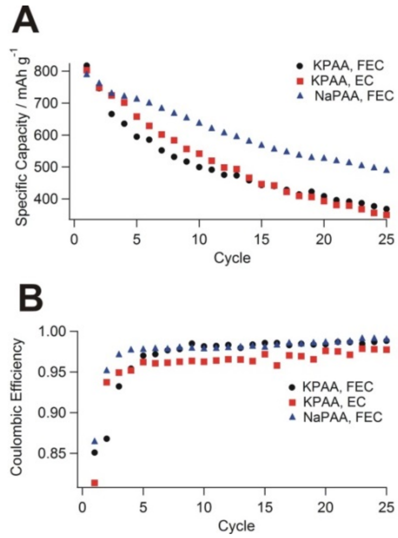

Figure 1. Cycling performance for different electrode systems. The data show changes associated with both the electrolyte, which contains either ethylene carbonate (EC) or fluoroethylene carbonate (FEC), and the different binders used for the electrodes.

Summary

In FY 2014, a manuscript examining the growth of the SEI using spectroscopic ellipsometry was published. In FY 2015, a more distinct push to investigate full electrode systems was undertaken; as part of the work, one manuscript has been submitted to a scientific journal, with a second in the final stages of preparation. The key technical achievements have been related to changes in performance associated with altering the binder used for electrode fabrication, the role that electrode density plays in minimizing performance degradation for advanced electrode systems, and the advancement of methods to understand morphological changes that happen in electrode structure during cycling. With respect to the use of different electrode conditions, Figure 1 shows changes that occur in cycling performance as different binders (potassium polyacrylate or sodium polyacrylate) are used to prepare a composite silicon/graphite electrode. This component of the project has found that not only do the binder and electrolyte play key roles in minimizing degradation for these composite systems, but that density is also a large factor in minimizing performance loss. A manuscript on this topic was recently submitted to the *Journal of Applied Electrochemistry*.

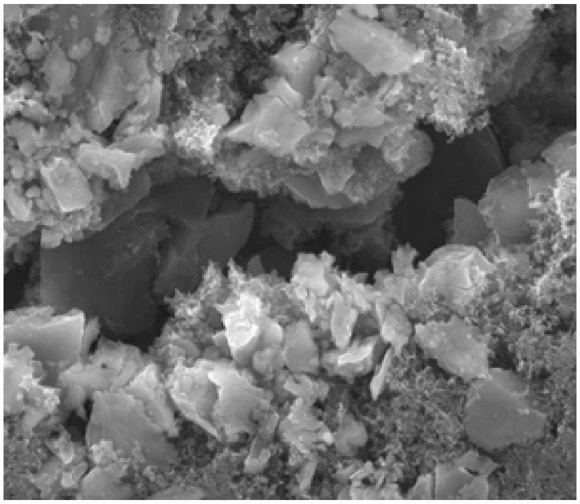

Figure 2. Image of an electrode prior to cycling. The portion of the electrode was chosen to highlight areas that are typically difficult to tie image processing and mechanical change algorithms.

The development of means to understand how the morphology of electrodes changes with cycling was the second major thrust in FY 2015. In this area, electrodes were imaged before and after cycling, and a protocol was developed to isolate different components of the electrode that could potentially undergo change during cycling. Figure 2 is a scanning electron microscope image one of the electrodes. The unique character of the crack in the electrode structure was mathematically treated such that the recessed portions of the electrode structure can be treated using the same algorithm as the outer portions without creating distortion. The implication of the work is that electrode images can now potentially serve as a means to build more refined electrochemical and mechanical models to predict battery performance.

Benefits to DOE

The ability to follow changes in the performance of electrode structures and the role that different conditions, including materials present and electrode densities, provides a means to engineer better-performing battery systems. A key to meeting the goals that DOE has set for electrification of the U.S. transportation fleet is in developing batteries that have higher energy and power densities. The current work looks to directly help with this focus by providing routes to understand how complete structures perform. Improving the electrification of transportation will improve environmental quality and help minimize the use of foreign energy sources. The means to process images and to understand the link between different components also helps advance the scientific missions of DOE.

Publications

Dufek, Eric J., “Evaluation of the SEI using a multilayer spectroscopic ellipsometry model,” *ECS Electrochemistry Letters*, Vol. 3, Issue 11, A108-A111, 2014.

Dufek, Eric J., Michael V. Glazoff, and Egor A. Shalashnikov, “Morphological Analysis and Synthesis for Understanding Electrode Microstructure Evolution as a Function of Applied Charge/Discharge Cycles,” in preparation.

Dufek, Eric J., Michael Picker, and Lucia M. Petkovic, “Density impact on performance of composite Si/graphite electrodes,” submitted to *Journal of Applied Electrochemistry*.

Presentations

Dufek, Eric J. and Lucia M. Petkovic, “Correlating electrochemical and spectroscopic ellipsometry signals to evaluate energy storage interfaces,” 224th Meeting of the Electrochemical Society, San Francisco, California, October 2013.

Dufek, Eric J., Michael V. Glazoff, and Kevin L. Gering, “Morphological analysis for the evaluation of electrode structures,” 224th Meeting of the Electrochemical Society, San Francisco, California, October 2013.

Dufek, Eric J., Lucia M. Petkovic, Harry W. Rollins, and John R. Klaehn, “Use of complementary methods to evaluate energy storage interfaces,” 248th National Meeting of the American Chemical Society, San Francisco, California, August 2014.

13-065—Multi-Domain Modeling, Simulation, and Integration Tools for the Dynamic Analysis and Optimization of Hybrid Energy Systems

Humberto E. Garcia, Jun Chen, Chris Paredis,[1] and William R. Binder[1]

The principal objective of this project is to develop (from formulation to verification/validation) dynamic modeling, integration, simulation, controls, and optimization (MISCO) capabilities for studying various aspects of hybrid energy systems (HESs). The purpose of this project is to develop the necessary computational tools and experience to enable the design, analysis, operation, and optimization of HESs using high-fidelity dynamic models and advanced simulation and optimization techniques. Specifically, the following capabilities were identified as being crucial to meeting the objectives of the project: dynamic modeling and simulation (M&S) tools (including creation of a modeling library to take advantage of model reusability); integration tools for synergizing the various tools and experiences available; optimization capabilities for both offline (design) and online (operations) optimization applications; and controls strategies, architectures, and algorithms to address new modern challenges such as the variability and uncertainty introduced by renewable sources and time-varying demands.

Summary

Progress in the MISCO capabilities toward meeting the objectives of this project includes the continued development of models and packages within a comprehensive Modelica-based library for HES research, development, and demonstration. This HES library takes advantage of the reusability of models to enable models of novel HES configurations to be effectively assembled and studied. In particular, numerous new models and modeling constructs were revised, developed, and further tested, including new models of renewable generation (including wind and photovoltaic solar), modulated thermal distribution centers, power cycles, controls, supervisors, operations optimizers, and control bus modules. Many of these computational capabilities were then integrated and utilized in HES studies. For example, a fuel cell battery model was built utilizing an existing Modelica-based fuel cell library (i.e., FCSys). This library is physics based, providing flexibility for reconfiguration, and also includes a special unit system that allows precise simulation in microscale. The fuel cell battery was built by stacking the cell model. For simplicity of computation, the assumption of uniform voltage/current over each cell was made, and accordingly the battery simulates one instance of the cell and multiplies the voltage/current output to mimic the stacking effect. A behavioral direct-current-to-direct-current converter was also built and provides constant voltage output based on power output from the fuel cell battery. In the domain of model integration, two platforms—the Functional Mockup Interface (FMI) and the Ptolomy II—have been successfully adopted and utilized in several analyses for model exchange and co-simulation. FMI has been used to obtain optimization results, and Ptolomy II has been successfully used to integrate Modelica-based thermo-electrical and Simulink models for co-simulation. Furthermore, the computational tool PSCAD with MathWorks tools (including Simulink) was integrated with Modelica-based models running in the M&S tool of Dymola. In particular, PSCAD was used to model and simulate electrical systems. Likewise, a preliminary tool for optimizing time-varying HES configurations with stochastic elements was developed using real option theory formulation, with results showing the relative impact of several variables on long-term profit and net present value metrics.

The computational developments realized from this project have been utilized to construct component and system models of several HES configurations and applied for different purposes such as parametric analysis, design/operations optimization, integration, and controls. For example, the computational capabilities developed

[1] Georgia Institute of Technology

under this project were crucial in supporting the unique results reported by Garcia et al.[2] The four key areas addressed are:

1. Technical Accomplishment 1: To properly analyze the variability in energy production and consumption, the project developed dynamic M&S tools, including Modelica libraries, unit models, and system models.
2. Technical Accomplishment 2: To address the variability in modeling, simulation, and M&S environments, the project investigated and demonstrated systems-integration tools, including model exchange (e.g., FMI/Functional Mockup Unit), co-simulation (e.g., Ptolemy II, Building Controls Test Bed, Dynamic Link Library), and non-real-time and real-time computational frameworks (e.g., Real-Time Digital Simulator).
3. Technical Accomplishment 3: To accordingly address the variability in components, configurations, and energy markets, the project developed design- and operations-optimization tools, including classical optimization, real-options optimization, and meta-modeling.
4. Technical Accomplishment 4: To effectively tackle the variability, uncertainty, and uncontrollability in energy production and consumption, the project implemented monitoring and control algorithms and tools, including local/global supervisory controls, operations optimizers, and predictive model controls.

From the studies conducted using the computational tools developed under this project, novel design and operational paradigms have been investigated, including:

- Integrated industrial-scale energy systems/microgrids with optimized designs, operations, and closely managed resources
- Reliable energy solutions that provide electricity to meet grid demands and ancillary needs with less energy storage
- New thermal energy options to alternative applications, while minimizing cycling of high-capital generators by employing thermal/electrical energy re-purposing in response to variability in net-load while operating at optimal profitability.

Benefits to DOE

HESs have been identified as a promising architecture for addressing the difficulties of integrating clean energy technologies into grid infrastructures and a key element in grid modernization. If successful, HESs could be a critical component of the nation's future energy portfolio, allowing use of clean energy technologies to expand and therefore reduce carbon emissions and other harmful environmental effects. Challenges include high variability and uncertainty in renewable resources and demands, grid instability arising from high levels of renewable penetration, and uncertainty in historical data combined with the high capital cost of nuclear plants. The MISCO capabilities developed under this project enable the types of analyses necessary to reduce risks from uncertainty and variability.

Publications

Binder, William R., Christiaan J. J. Paredis, and Humberto E. Garcia, "Design Optimization of a Hybrid Energy System Using Real Options," in preparation.

Chen, J. and H. E. Garcia, "Economic optimization of operations for hybrid energy systems under variable markets," *IEEE Transactions on Power Systems*, submitted and in review.

[2] H. E. Garcia, J. Chen, J. S. Kim, M. G. McKellar, W. R. Deason, R. B. Vilim, S. M. Bragg-Sittion, and R. D. Boardman, "Nuclear Hybrid Energy Systems - Regional Studies: West Texas & Northeastern Arizona," INL/EXT-15-34505, April 2015.

Chen, J. and H. E. Garcia, "Operations optimization of hybrid energy systems under variable markets," American Control Conference (ACC), submitted and in review.

Chen, J., H. E. Garcia, J. S. Kim, and Shannon Bragg-Sitton, "Operations optimization of nuclear hybrid energy systems," *Nuclear Technology*, submitted and in review.

Garcia, H. E., J. Chen, J. S. Kim, et al., "Dynamic Performance Analysis of Two Regional Nuclear Hybrid Energy Systems," *Energy*, submitted and in review.

Garcia, H. E., J. Chen, J. S. Kim, M. G. McKellar, W. R. Deason, R. B. Vilim, S. M. Bragg-Sitton, and R. D. Boardman, "Nuclear Hybrid Energy Systems - Regional Studies: West Texas & Northeastern Arizona," INL/EXT-15-34505, April 2015.

Kim, J. S., J. Chen, and H. E. Garcia, "Modeling, control, and dynamic performance analysis of a reverse osmosis desalination plant integrated within hybrid energy systems," *Energy*, submitted and in review.

Kim, J. S. and H. E. Garcia, "Nuclear-Renewable Hybrid Energy System for Reverse Osmosis Desalination Process," *Proceedings of the 2015 American Nuclear Society Annual Meeting*, San Antonio, Texas, June 7-11, Vol. 112, pp. 121–124, 2015.

Presentations

Du, Wenbo, Humberto E. Garcia (presenter), William R. Binder, and Christiaan J. J. Paredis, "Value-Driven Design and Sensitivity Analysis of Hybrid Energy Systems Using Surrogate Modeling," International Conference on Renewable Energy Research and Applications, October 21, 2014.

Garcia, Humberto E., "Energy Systems Integration: At-scale Integrated Engineering Design for Active Energy Efficiency Management," Center for Advanced Energy Studies Meet and Greet Event, January 8, 2015.

Garcia, Humberto E., "Dynamic Systems Integration, Optimization, and Resilient Controls," Oregon State University Meeting, February 17, 2015.

Garcia, Humberto E., "Design Optimization, Operations Optimization, Dynamic Simulation and Controls," Oak Ridge National Laboratory Meeting, April 29, 2015, and National Renewable Energy Laboratory Meeting, February 23–24, 2015.

Garcia, Humberto E., "Hybrid Energy Systems: Design/Operations Optimization, Dynamic Simulation and Controls," Nuclear Energy Agency Visit, Paris, France, September 24, 2015.

Garcia, Humberto E., "Hybrid Energy Systems: Design/Operations Optimization, Dynamic Simulation and Controls," Meeting at University of Wyoming, August 12, 2015.

13-068—Cooling in Fractured Geothermal Reservoirs: Analyses of Long-Term Cooling in Typical Geothermal Reservoirs and Application to Geothermal Resource Potential

Mitchell Plummer, Michael McCurry,[1] John Welhan,[2] Thomas Wood,[2] Carl Palmer,[2] John Brouwer,[3] Alex Moody,[2] Jerry Fairley,[2] and Timothy Ronan[4]

The initial objectives of this project were to (a) develop a tool to estimate long-term geothermal reservoir capacity based on limited information about fracture distribution and geometry and (b) apply that tool to data from the eastern Snake River Plain (ESRP) to provide physical and hydraulic constraints on reservoir characteristics suitable for enhanced geothermal system (EGS) development. Following an INL and Center for Advanced Energy Studies (CAES) institutional commitment to propose INL as the site for the DOE Geothermal Technology Office's future EGS field laboratory (the FORGE site), this project was redirected to provide scientific studies focused on geothermal characteristics of the ESRP.

Summary

This LDRD supported INL and CAES university research related to cooling in fractured geothermal reservoirs. Undergraduate internship students from Boise State University and the University of Wyoming completed projects, including:

- Development of a MATLAB interface for semi-analytical solutions to flow and heat transport equations for fracture flow. Timothy Ronan was selected as a Boise State University CAES Energy Scholar for this work.
- Development of a Microsoft Access and ArcGIS project that queried groundwater temperature records for the ESRP and performed statistical analyses of, and contoured, selected data for use as a reference in a groundwater heat-transport modeling study aimed at better understanding heat fluxes beneath the ESRP.

Collaborator Jerry Fairley, at the University of Idaho, supported a master's degree student, Alex Moody, who completed an extensive analysis of fracture distribution in rock cores from deep wells in the Snake River Plain and submitted a manuscript (in second review) to the *Geological Society of America Special Publication on Geothermal Energy*.

To provide improved understanding of geothermal conditions in the ESRP, this project supported studies of geology, geochemistry, and heat transport with collaborations at Idaho State University and of the University of Idaho:

- Michael McCurry integrated and analyzed existing geologic data in order to develop more robust, testable models of the reservoir geology of the ESRP. This effort produced a digital compendium of geologic data regarding the ESRP and new cross-section models of the subsurface geologic architecture, materials, and processes in regions targeted as INL's field EGS laboratory.
- Dr. John Welhan examined the temperature and chemistry of thermally influenced groundwater in the ESRP to determine how such information may be used to identify areas of upward advective heat transport into the ESRP aquifer. Waters that are chemically labeled by reaction with rhyolitic rocks at elevated temperature were confirmed to recharge the aquifer, demonstrating that advective heat transfer needs to be considered

[1] Idaho State University

[2] University of Idaho

[3] University of Wyoming

[4] Boise State University

when modeling heat transport in the aquifer. The spatial variability and low signal/noise ratio of tracer concentrations in the aquifer, however, greatly limits their utility in identifying where such inputs occur.

- Mitchell Plummer and University of Idaho collaborators completed development of a three-dimensional heat-transport model of the ESRP aquifer based on the Eastern Snake Hydrologic Modeling Committee's groundwater flow model. Solving advection and dispersion equations for heat transport, the model illustrates how groundwater flow interacts with vertical geothermal heat fluxes to produce complex temperature distributions in the aquifer (Figure 1). Important conclusions include:
  - Isolated zones of significantly higher groundwater temperatures in the middle of the aquifer can be developed where groundwater velocities are low. That is, large horizontal gradients in groundwater temperature are likely the result of contrasts in water flux, not variations in the geothermal heat flux.
  - Vertical temperature profiles within the aquifer are strongly controlled by horizontal groundwater flux and vertical mixing. Commonly observed isothermal temperature profiles indicate that mechanical dispersion is relatively large.
  - Heat flux through the vadose zone, though generally a weak control on groundwater temperature, can create regions of higher or lower temperature at the top of the aquifer.

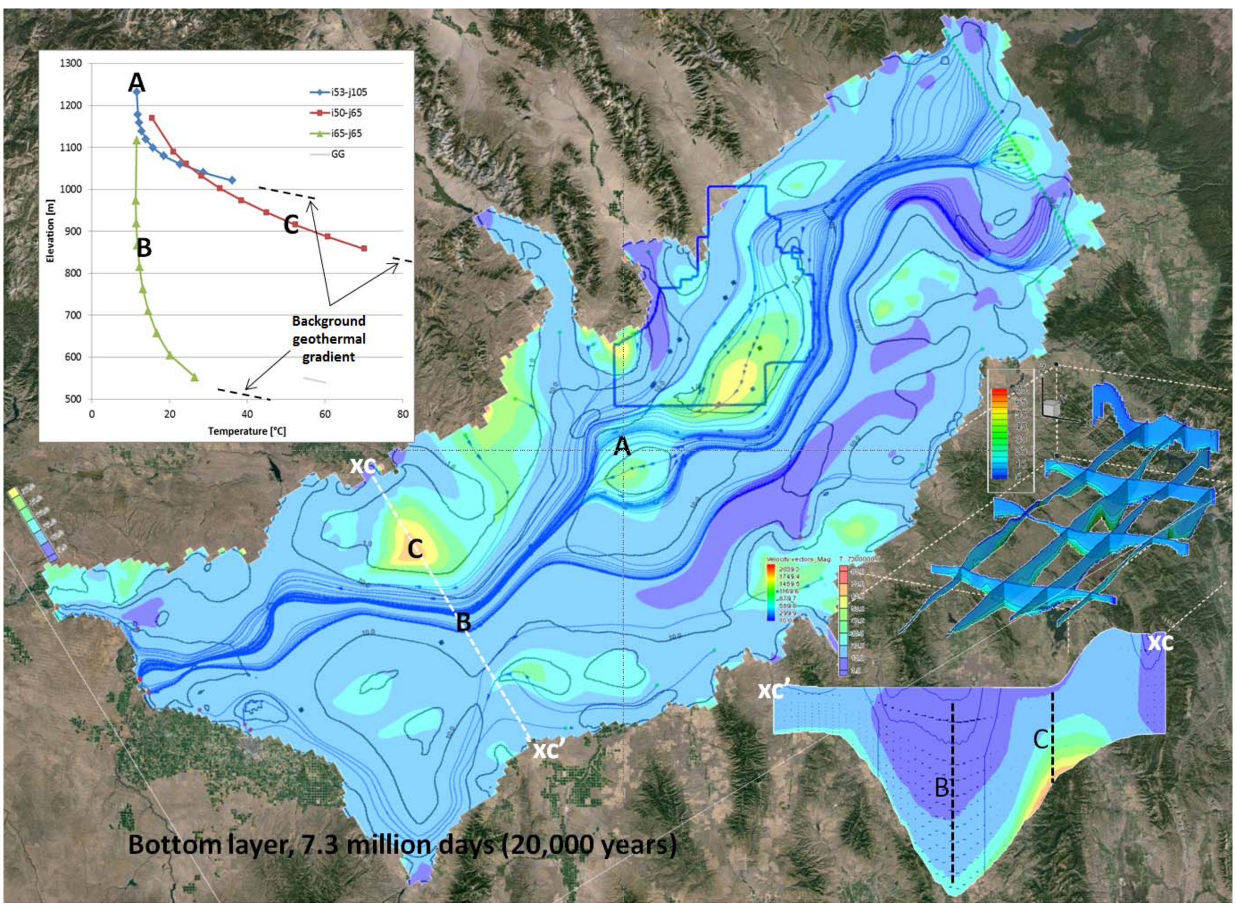

Figure 1. Temperature map of the bottom of the ESRP aquifer based on heat transport simulations conducted for this study. Color bands show temperature [°C]; black lines give horizontal water flux magnitude [m/day]; and blue lines are selected stream lines. Inset cross sections (far right) illustrate aquifer shape and, at xc-xc', geothermal heat flux impact in low-velocity zones. The inset plot of temperature profiles (upper left) illustrates how velocity acts to control the shape of vertical temperature profiles.

Benefits to DOE

The development of engineered geothermal systems could play a substantial role in DOE's mission to bring new clean energy sources to market. INL has been selected as one of several sites that may host a major DOE facility aimed at testing EGS concepts and methods, which could lead to significant increases in geothermal energy generation. Through scientific study of the geologic and physical controls on temperature and geomechanical conditions in the ESRP, this project advances INL's goal of becoming a leader in EGS science and providing a proving ground for its development. The groundwater heat-transport modeling conducted is an innovative means of examining geothermal heat flux variability that also provides feedback about groundwater flow parameters not easily obtained via other methods.

Publications

Moody, A., J. Fairley, and M. Plummer, "Stochastic exploration and the geologic context of enhanced geothermal system viability on the Snake River Plain, Idaho" *Geological Society of America Special Papers: Geothermal Energy: An Emerging Resource*, in press.

Plummer, M., "Insights into Cold Water Injection Stimulation Effects through Analytical Solutions to Flow and Heat Transport," *Geothermal Resources Council Transactions*, Vol. 37, 2013.

Welhan, J., "Thermal and Trace-Element Anomalies in the Eastern Snake River Plain Aquifer: Toward a Conceptual Model of the EGS Resource," *Geothermal Resources Council Transactions*, Vol. 39, 2015.

Welhan, J., M. Gwyn, S. Payne, M. McCurry, M. Plummer, and T. Wood, "The Blackfoot Volcanic Field, Southeast Idaho: A Hidden High Temperature Geothermal Resource in the Idaho Thrust Belt," SGP TR 202, *Proceedings, Thirty-Ninth Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, February 24–26, 2014.

Presentations

Moody, A., J. Fairley, and M. Plummer, "Theoretical Fracturing and Power Production from Low Permeability Tuffs in the Snake River Plain, Southern Idaho," Paper No. 338 5, 2013 Geological Society of America Annual Meeting, Denver, Colorado, 2013.

Plummer, M., "Insights into Cold Water Injection Stimulation Effects through Analytical Solutions to Flow and Heat Transport," Geothermal Resources Council Annual Meeting, Las Vegas, Nevada, 2013.

Plummer, M., K. Smith, and R. Podgorney, "Cold Water Injection Effects in Fractured Reservoirs," Paper No. 387 10, 2013 Geological Society of America Annual Meeting, Denver, Colorado, 2013.

13-079—Diverse Biological Factories for Sustainable Manufacturing

Dayna L. Daubaras

This project supports the DOE Advanced Manufacturing Office's search for innovative, energy-efficient chemical manufacturing. This project is creating unique biological tools and organisms for biochemical conversions to enable the energy-efficient production of commodity chemicals, fine chemicals, and fuels. Biological systems can be engineered to convert inexpensive carbon sources to chemical intermediates that can undergo additional chemical catalysis to chemicals and fuels. Currently, only a few organisms are available for genetic engineering and large-scale production, under a limited set of growth and conversion conditions. These common industrial organisms require expensive carbon sources for growth and extensive engineering to modify their central metabolic pathways, often resulting in low titers. The focus of this LDRD is to identify organisms with native metabolic pathways that can be minimally manipulated through synthetic biology and use less expensive carbon sources for economical chemical production. The selected hosts should function under extreme conditions to align with industrial processes, grow under conditions that maintain sterile processes, and facilitate energy-efficient product recovery. The chemicals this project proposes to target are those currently sourced from petroleum resources and energy-intensive chemical processes.

Summary

In the first year of the project, a halophile was selected for the production of isoprenoid compounds using the inherent mevalonate metabolic pathway to provide the appropriate intermediates for biochemical conversions. The target organism was engineered using synthetic DNA technology. Specifically, two plant isoprene synthase genes were synthetically designed and introduced on multicopy plasmids into the organism. The synthetic design was a cassette-based system with regulatory control elements for rapid design and testing of additional synthetic terpenoid synthase genes. An added benefit to the system was the deletion of the host gene encoding phytoene synthase, which stopped the production of bacterioruberin, the orange-red colored carotenoid. This genetic modification served two purposes: (a) to divert metabolic intermediates from carotenoid production to the synthetic plant isoprene synthase enzymes and (b) to generate a colorimetric screening tool for introducing synthetic genes on the host chromosome (the deletion strain is colorless). Unfortunately, isoprene production could not be detected using two different synthetic plant isoprene synthase genes inserted on the plasmid or chromosome. However, the colorless deletion strain for future studies was created.

In the second year of the project, the plasmid-based cassette system generated during the first year was tested. The polymerase chain reaction was used to amplify the host phytoene synthase gene and reintroduced it to the deletion strain, using the plasmid-based cassette and replacing the synthetic isoprene synthase gene. The introduced phytoene synthase gene restored bacterioruberin production at levels up to four-fold higher than the original host strain. This result confirms that the terpenoid expression cassette engineered on the multicopy plasmid has the capacity to overproduce enzymes involved in isoprenoid production.

In the third year, alternate plant terpene synthase-encoding genes were designed specifically for the production of pinene. The first synthetic design was a plant pinene synthase gene replacing the isoprene synthase gene on the plasmid cassette, and the second synthetic design was a fusion protein with a truncated pinene synthase fused to the host geranyl-geranyl-pyrophosphate synthase, which generates the intermediate for the enzyme pinene synthase. The rationale for the second design was to generate increased intermediates from the geranyl-geranyl pyrophosphate synthase directly to the pinene synthase enzyme and to aid the production of pinene synthase by making it dependent on the geranyl-geranyl pyrophosphate synthase production. Unfortunately, this fusion protein production was inconclusive, and pinene production could not be detected. In summary, a colorimetric system for identification of genetic modifications to the host strain, an important step required for rapid screening, was created and tested. The interchangeable genetic modifications created are versatile enough to easily replace the current synthetic catalyst, isoprene synthase, with other valuable catalysts.

Benefits to DOE

Creating production strains using diverse organisms for industrial scale-up processes will increase energy efficiency in chemical production. This type of biochemical conversion to intermediates can have a long-term positive impact on our nation's dependence on foreign oil. Many biological processes are considered more environmentally friendly due to the decreased use of energy in scale-up processes, the reduction in CO_2 emissions compared to chemical processes, and the value added to a primary process by using otherwise "waste" products as biological substrates for growth. Reducing dependence on foreign oil by generating hydrocarbon compounds through biological processes can be invaluable to national energy security.

Publications

A manuscript is in preparation for submission the beginning of FY 2016.

Presentations

Daubaras, D. L., "Biological Factories for Sustainable Manufacturing," INL Energy Environment Science & Technology (EES&T) Biological Sciences Seminar Series, Idaho Falls, Idaho, May 8, 2015.

Daubaras, D. L., D. W. Reed, and H. G. Silverman, "Diverse Biological Factories for Sustainable Manufacturing," INL Annual LDRD 2015 Poster Session, Idaho Falls, Idaho, October 15, 2015.

13-110—Nuclear-Renewable-Oil Shale Hybrid Energy System

Humberto E. Garcia, Charles Forsberg,[1] Daniel Curtis,[1] Robert Cherry, and Mike McKellar

Nuclear renewable oil shale systems (NROSSs) constitute a class of large hybrid energy systems (HESs) in which nuclear reactors provide the primary energy used to produce shale oil from kerogen deposits and also provide flexible, dispatchable electricity to the grid. Kerogen is solid organic matter trapped in sedimentary shale, and the formations of kerogen oil shale in the western United States are the largest and densest hydrocarbon resource on the planet. When heated above 300°C, kerogen decomposes into oil, gas, and char. An NROSS couples electricity and transportation fuel production in a single operation, reduces life-cycle carbon emissions from the fuel produced, improves economics for the nuclear plant, and enables a major shift toward a very low-carbon electricity grid. Thus, the project objectives are as follows:

1. Describe the general strategic motivation for developing a large energy system to address the challenges of producing a very low-carbon energy supply and secure hydrocarbon supply, and describe the specific strategic motivation for developing an NROSS.
2. Design the plant configuration of an NROSS that accomplishes the goals listed in Item 1 above.
3. Analyze a selection of NROSS performance measures chosen to demonstrate the value and viability of the system concept.
4. Describe the necessary R&D efforts, institutional partnerships, demonstration systems, and commercialization activities (collectively, a "development pathway") necessary to deploy NROSS.

Summary

The analysis conducted during this project has shown that liquid fuels produced by a baseline NROSS would have a lower life-cycle greenhouse gas impact than any available fossil liquid fuels and that operation as part of an NROSS complex would increase reactor revenues relative to a stand-alone baseload reactor. The flexible, dispatchable electricity provided by an NROSS could also enable the transition to a very low-carbon grid in which renewables are widely deployed and the NROSS provides variable output to balance the renewables' uncontrolled output. Large-scale deployment of NROSSs will be an enormous undertaking, requiring substantial resources and involvement from a large and complex array of organizations, but the effort will reduce carbon emissions from both the electric-power and transportation sectors, reduce U.S. reliance on foreign energy resources, and accelerate the transition to a cleaner, more efficient, and more reliable energy system. The main challenges addressed by this project include the following:

- Integrate intermittent renewable generators in the future very-low-carbon grid
- Satisfy electricity demand at all times
- Deliver heat to oil shale in situ
- Configure complex facilities for combined nuclear and oilfield operations.

The main approach and novelty associated with this project may be grouped as follows:

- Deregulated electricity real-time-market data-driven analysis
- Advance greenhouse gas emissions life-cycle assessment
- Design the power plants for high lifetime utilization of capital assets

[1] Massachusetts Institute of Technology

- Configure a complex facility for combined nuclear and oilfield operations
- Couple previously independent energy markets—electricity and fuel production
- Improve U.S. energy security through utilization of a large domestic resource, i.e., oil shale.

Two key results follow from a case study in which the nuclear plant is located in Colorado, supplies steam to an adjacent in situ oil-shale-production operation, is owned by an entity separate from the petroleum system operator, and supplies electricity to the California independent system operator market:

- Revenue for the nuclear plant increases by 41%
- CO_2 per unit of liquid fuel produced is 36% less than the most mature alternative in situ oil-shale-production method, i.e., the Shell In Situ Conversion Process.

A second case study, in which the reactor and petroleum system are owned by a single entity, suggested that, with a goal to maximize full-system revenue, nearly all reactor energy would be directed to maximizing the oil production rate at $100 per barrel, and energy would only be directed to electricity production less than 5% of the time. Sensitivity studies showed that electricity production would not rise above 10% with a revenue optimization objective until oil prices had fallen below $35 per barrel. The most important recommendation for future work is the prompt creation of a cross-cutting program to develop a strategy and methods for safety certification of process heat delivery systems, an essential component of an NROSS, many other HESs, and many commercialization strategies for Generation IV reactors.

Benefits to DOE

This project proposed a hybrid energy system that would make use of a large domestic energy resource (kerogen oil shale) to simultaneously improve nuclear power plant economic performance, improve U.S. energy security, and reduce the environmental quality impacts that might be incurred by producing kerogen oil shale by different means.

Publications

Curtis, Daniel, *Nuclear Renewable Oil Shale Hybrid Energy System: Configuration, Performance, and Development Pathway*, M.S. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, February 2015.

Curtis, Daniel, Charles Forsberg, and Humberto Garcia, “Development of Nuclear Renewable Oil Shale Systems for Flexible Electricity and Reduced Fossil Fuel Emissions,” *Proceedings of the 2015 International Congress on Advances in Nuclear Power Plants (ICAPP)*, Paper No. 15180, Madrid Polytechnic University, Spain, May 2015.

Curtis, Daniel, Charles Forsberg, Michael McKellar, and Earl Mattson, “A Demonstration Project Coupling a Small Modular Reactor with a Hybrid Nuclear Renewable Oil Shale System,” *Proceedings of the 2014 International Congress on Advances in Nuclear Power Plants,* Paper No. 14057, Charlotte, North Carolina, April 6–9, 2014.

Presentations

Curtis, Daniel and Charles Forsberg, “Light-Water-Reactor Arrays for Production of Shale Oil and Variable Electricity,” American Nuclear Society 2013 Annual Meeting, Atlanta, Georgia, June 16–20, 2013.

Curtis, Daniel and Charles Forsberg, “Nuclear Renewable Oil Shale System Development Pathway,” ANS 2015 Annual Meeting, San Antonio, Texas, June 7–11, 2015.

Curtis, Daniel and Charles Forsberg, "Nuclear Heat and Power for In-situ Oil Production and Variable Electricity," 33rd Oil Shale Symposium, Golden, Colorado, October 14–16, 2013.

Curtis, Daniel and Charles Forsberg, "Nuclear Oil Shale – Partnership Opportunity for an Expanded Domestic SMR Market," *American Nuclear Society 2013 Winter Meeting and Technology Expo*, Washington, D.C., November 10–14, 2013.

Curtis, Daniel, Charles Forsberg, and Humberto Garcia, "Development of Nuclear Renewable Oil Shale Systems for Flexible Electricity and Reduced Fossil Fuel Emissions," International Congress on Advances in Nuclear Power Plants (ICAPP), Nice, France, May 3–6, 2015.

Curtis, Daniel, Charles Forsberg, and Andrew Kadak, "Production of Shale Oil and Variable Electricity that Enables Use of Wind Resources Using Light-Water and High-Temperature Reactors," International Oil Shale Symposium 2013, Tallinn, Estonia, June 10–13, 2013.

Curtis, Daniel, Charles Forsberg, Michael McKellar, and Earl Mattson, "A Demonstration Project Coupling a Small Modular Reactor with a Hybrid Nuclear Renewable Oil Shale System," 2014 International Congress on Advances in Nuclear Power Plants, Charlotte, North Carolina, April 6–9, 2014.

Forsberg, Charles and Daniel Curtis, "Nuclear Renewable Oil Shale System (NROSS) – Making Oil Shale the Fossil Fuel with the Lowest Greenhouse Impact per Liter of Diesel or Gasoline While Improving Economics," 34th Oil Shale Symposium, Golden, Colorado, October 13–15, 2014.

14-078—Extended Stability Gamma-Gamma Prime Containing Nickel-Base Alloys

Subhashish Meher, Laura J. Carroll, Mark C. Carroll, and Tresa M. Pollock[1]

Power generation through concentrating solar, nuclear, and fossil energy continues to demand improved efficiencies to remain competitive. In each case, these increasing efficiencies require materials that exceed the properties of the available state of the art. Fortunately, the material requirements of the specific hot-section components from three industries are similar: an extended-stability alloy capable of operating at 1,000°C for up to 100,000 hours, either to extract the maximum amount of efficiency from the system or to make the system technologically feasible with regard to its intended purpose. The objective of the proposed work is to develop a γ-γ' nickel-base superalloy that is capable of meeting these requirements and is microstructurally stable with regard to secondary-phase composition and distribution. A stable microstructure will result in an alloy with a consistent set of mechanical properties at elevated temperatures. The objective of this program is to dramatically improve the stability of γ-γ' superalloys through specific control of the composition of nickel-base superalloys by controlled partitioning coupled with targeted processing.

Summary

In the current project, three classes of superalloys are being investigated: nickel-base, nickel-chromium-base, and cobalt-base. The objectives include (a) detailed microstructural characterization of all three classes of alloys at multiple-length scales following high-temperature exposure and (b) the integration of critical experimental inputs for the utilization of a computational kinetic-modeling tool to simulate the microstructure of experimental superalloys subjected to high temperatures (Figure 1). The combinatorial approach of experiments and state-of-the-art modeling are greatly beneficial for the superalloy design.

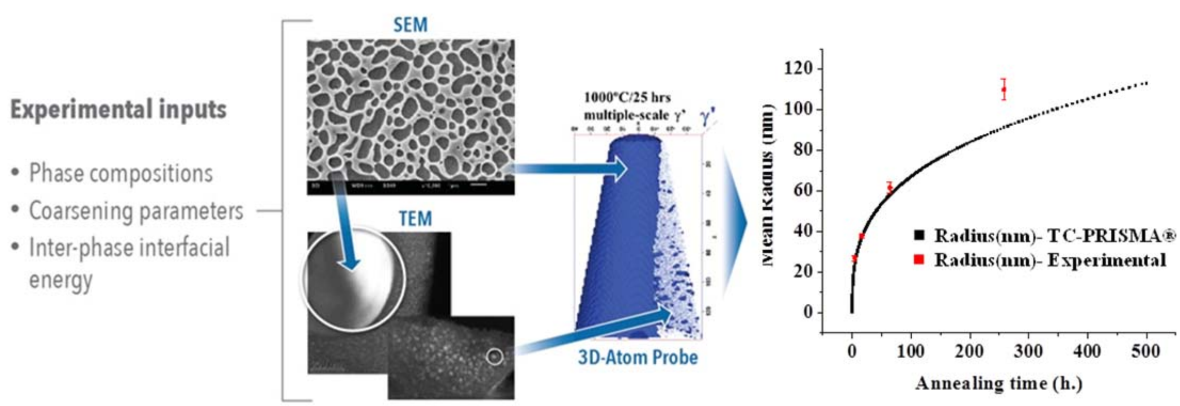

Figure 1. Diagram of multiscale characterization methods and incorporation of critical experimental parameters to a kinetics-modeling tool for simulation of long-term microstructural stability.

For all of the experimental alloys, characterization of the phase compositions, as well as precipitate volume fraction, size, and shape after aging, was completed utilizing transmission electron microscopy, scanning electron microscopy, and atom probe tomography. Kinetic modeling was carried out with CALPHAD-based TC-PRISMA modeling software. Precipitate coarsening was investigated to assess the stability kinetics in comparison to currently available superalloys, and coarsening rates were found to be lower than typically observed. Interestingly, in the specific range of alloy chemistry and processing temperature, multiple-phase transformation

[1] High Temperature Metals Consulting

pathways were observed. The governing factors for coarsening have been identified through analysis of the experimental data and are in the process of being verified with modeling techniques.

Benefits to DOE

This project is developing an alloying/microstructural strategy for γ-γ' superalloys. These superalloys have inherent long-term stability due to tailored, unique microstructures that make them ideal for extended service at the high temperatures necessary for use in specific solar-/fossil-/nuclear-energy components, thus enabling increased efficiencies and energy production. Currently, the state-of-the-art materials available for very high-temperature structural applications are limited in either strength or duration of service due to an evolving γ' microstructure. In line with the DOE-NE initiatives for advanced, next-generation, high-temperature nuclear reactors, higher outlet temperatures drive overall increased efficiency and the potential for utilization of process heat. Deployment of nickel-base superalloys in a number of targeted components would be the catalyst for further increasing reactor outlet temperatures and extracting additional efficiency from the cycle.

Publications

Meher, S., L. J. Carroll, T. M. Pollock, and M. C. Carroll, "Coarsening kinetics of γ' precipitates in near zero lattice misfit nickel-base superalloys," in preparation.

Meher, S., M. C. Carroll, T. M. Pollock, and L. J. Carroll, "Co-existence of γ and γ' precipitates in Ru and Re containing nickel-base superalloys," in preparation.

Meher, S., M. C. Carroll, T. M. Pollock, and L. J. Carroll, "Solute partitioning in multi-component γ/γ' CoNi-base superalloys with near zero lattice misfit," submitted to *Scripta Materialia*.

Meher, S., L. J. Carroll, T. M. Pollock, and M. C. Carroll, "Stability of multiple generation of γ' precipitates in high Ru and Re containing nickel-base superalloys," in preparation.

Presentations

Meher, S., "Atomic scale observation of the structure and composition of γ/γ' interfaces and solute partitioning across these interfaces in cobalt-base alloys," International Workshop on Advanced Co-based Superalloys, Gaithersburg, Maryland, June 23–24, 2015.

Meher, S., "Extended microstructural stability in high refractory containing nickel-base superalloys," TMS 2015 144th Annual Meeting & Exhibition, Orlando, Florida, March 15–19, 2015.

14-079—Second-Generation Switchable Polarity Solvent Draw Solutes for Forward Osmosis

Aaron D. Wilson, Christopher J. Orme, Josh McNally, Frederick F. Stewart, and Jeffrey R. McCutcheon[1]

The switchable polarity solvent (SPS) forward osmosis (FO) process can purify water from extremely concentrated feeds containing components such as salts, organics, inorganics, and biologics. INL has demonstrated that a dimethylcyclohexylamine SPS draw solution can provide osmotic flux against a 226,000 ppm total dissolved solid NaCl solution. SPS FO functions at a fraction (<0.5) of the cost of existing methods through a thermolytic cycle that avoids the distillation of water but still uses heat energy—heat that costs a fraction of electrical energy used in reverse osmosis. The drawback of this initial demonstration of SPS FO is the aggressive solvent characteristics of dimethylcyclohexylamine, which damages membranes and a wide range of rubbers and plastics. Advancement of SPS FO to industrial implementation requires an SPS that retains the high osmotic pressures of dimethylcyclohexylamine without the material incompatibilities. In this project, materials will be developed as draw solutes for FO systems that have high osmotic pressures, low viscosities, and reasonable costs. These materials will require properties similar to previously studied materials while avoiding material degradation, reducing toxicity, reducing membrane permeation, and improving SPS switching behavior. This work will include the synthesizing and characterization of amines. With a viable SPS, an integrated demonstration of an SPS FO process will be developed based on the most effective SPS candidate.

Summary

The first effort in this project was to complete and publish a structure-function model of the SPS's capability to form concentrated solutions. This structure function model allowed the Generation II SPS class to be identified based on 1-cyclohexylpiperidine (CHP). CHP has a higher molecular weight than the SPS used to demonstrate the SPS FO process. The higher molecular weight provides a number of advantages, including (a) reduced vapor pressure/odor; (b) better kinetics, lower temperatures, and more complete polar-to-nonpolar phase transitions (degassing); (c) lower water solubility in the nonpolar form; (d) better materials compatibility; and (e) lower likelihood of passing through membranes for FO/reverse osmosis applications. The Generation II SPS adds all of these advantages while retaining the high osmotic pressure and low production cost of *N,N*-dimethylcyclohexylamines. Battelle Energy Alliance, LLC, has submitted a patent application (BA-808) for the use of Generation II SPS in FO water treatment. The researchers on this project then published a paper highlighting the draw solute performance metrics of CHP. This work was a followed up with a computational chemistry density functional theory study by Joshua McNally to identify and understand the intramolecular structures that influenced intermolecular and inter-ion interactions that produce bulk properties and behaviors. Dr. McNally has since been transitioned to a full-time staff member, in part due to his work on this project.

A concentration dependent study of Generation II and two control SPSs was also conducted. This work has resulted in a published paper addressing mass transport properties and solution-state speciation, generalized to all SPSs. These concentration-dependent properties are fundamental to process design and optimization of any application of SPS.

Also, (±)-*trans-N,N,N',N'*-tertamethyl-1,2-diaminocyclohexane was generated at the 300-g scale and demonstrated to be effective SPS materials. The diamine can reach 80 wt% in its polar form before forming a crystalline material, matching the performance of the best monoamines. In the next year, concentration performance metrics will be obtained for the diamine and compared to the Generation II SPS.

[1] University of Connecticut

The collaboration with Jeffery McCutcheon at the University of Connecticut has yielded two significant results. The first was an analysis of the fundamentals of energy associated with pressure-retarded osmosis (PRO) and removing/concentrating total dissolved solid from/in a solution. The second was a membrane/ SPS compatibility that addressed water flux data, reverse solute flux, and solute/membrane parameters for several membranes.

Previously, the project obtained an x-ray crystal structure of a *N,N*-dimethylcyclohexylammonium bicarbonate. This structure featured a hydrogen-bonded bicarbonate dimer. Recently, Frank Weinhold and Roger Klein at the University of Wisconsin proposed the existence of anti-electrostatic hydrogen-bond complexes that would conclusively demonstrate a dominant covalent component of the hydrogen bond. The bicarbonate dimer is an example of an anti-electrostatic hydrogen bond and, based on a variety of experimental evidence, appears to be present in the solution state. This would be the first example of an anti-electrostatic hydrogen-bond complex found in solution. Dr. McNally traveled to the Oak Ridge National Laboratory Spallation Neutron Source User Facility to obtain a neutron structure of the project's bicarbonate dimer. The results should influence the project's understanding of the hydrogen bond. This understanding will have a wide impact on chemistry from the classroom to the research laboratory.

Based on the published work (including papers from this LDRD) by the project's researchers, they were contacted by a startup business, Rebound Technologies, working in the field of modest- to large-scale refrigeration. The interaction with Rebound Technologies developed into a collaboration that resulted in a funded Phase I Small Business Technology Transfer project. This collaboration is built around a new field of use for SPS that would not have been possible without the fundamental work developed in this LDRD.

In addition to the transition of Dr. McNally to a full-time employee, there have been two recent hires relevant to developing and expanding INL staff. Birendra Adhikari, a chemical engineer from Colorado University at Boulder (2015), and undergraduate Catherine Hrbac, a chemical engineer from the Massachusetts Institute of Technology (2015), were hired through this LDRD to expand the project's expertise in chemical engineering. Their chemical engineering skills are required for developing fundamentals processes associated with SPS FO and other water-treatment technologies.

Benefits to the DOE

Water treatment and desalination are energy-intensive processes with room for improvement. Reducing this energy cost would meet DOE's mission, but the connection between water and energy runs deeper. The current energy infrastructure requires water to produce energy (evaporative cooling, biomass and algae production) and obtain energy resources (well injection [fracing] water). Water used by the energy industries eventually requires treatment (oil and gas water, blowdown water, and many others). The timeliness of this work is well illustrated by the issues at Turkey Point Nuclear Generating Station and the nationwide drought conditions, especially those in California's central valley. Mission impact beyond DOE would be best described in terms of energy, water, and food security. The technology under development may also have application for water production at forward operating military bases. This project is expected to develop scalable water-treatment technology that can reduce the cost of producing and processing water relevant to the energy industry and military.

SPSs constitute a rapidly developing field of research. The current work allows the researchers on this project to advance their application to water treatment and other fields of use, as well as publish fundamental work on SPSs that have implications on very fundamental concepts, including electrolyte theory and the hydrogen bond. This work helps to achieve DOE science and applied missions.

Publications

McNally, J. S. and A. D. Wilson, "Density Functional Theory Analysis of Steric Impacts on Switchable Polarity Solvent (SPS)," *Journal of Chemical Physics B*, Vol. 119, pp. 6766–6775, DOI: 10.1021/acs.jpcb.5b03167, 2015.

Orme, C. J. and A. D. Wilson, "1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Engineered Osmosis," *Desalination*, Vol. 371, pp. 126–133, DOI: 10.1016/j.desal.2015.05.024, 2015.

Reimund, K. K., B. J. Coscia, J. T. Arena, A. D. Wilson, and J. R. McCutcheon, "Characterization and Membrane Stability Study for the Switchable Polarity Solvent N,N-Dimethylcyclohexylamine as a Draw Solute in Forward Osmosis," *Journal of Membrane Science*, in review.

Reimund, K. K., J. R. McCutcheon, F. F. Stewart, and A. D. Wilson, "Thermodynamic analysis of energy density in pressure retarded osmosis: The impact of solution volumes and costs," *Journal of Membrane Science*, Vol. 487, pp. 240–248, DOI: 10.1016/j.memsci.2015.03.076, 2015.

Wilson, A. D. and F. F. Stewart, "Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents," *RCS Advances*, Vol. 4, pp. 11039–11049, 2014.

Wilson, A. D. and C. J. Orme, "Concentration Dependent Speciation and Mass Transport Properties of Switchable Polarity Solvents," *RCS Advances*, Vol. 5, pp. 7740–7751, DOI: 10.1039/C4RA08558B, 2015.

Presentations

Orme, C. J., J. S. McNally, D. S. Wendt, and A. D. Wilson, "1-Cyclohexylpiperidine-CO_2 Switchable Polarity Solvent (SPS) Draw Solution Performance Results," North American Membrane Society (NAMS) 25th Annual Meeting, Boston, Massachusetts, June 2015.

Reimund, K., B. Coscia, A. Wilson, and J. McCutcheon, "Forward Osmosis Flux Performance and Membrane Compatibility Studies of the Dimethylcyclohexyl Ammonium Hydrogen Carbonate Switchable Polarity Solvent (SPS) Draw Solute," North American Membrane Society (NAMS) 24th Annual Meeting, Houston, Texas, June 2014.

Wendt, D. S., G. L. Mines, C. J. Orme, and A. D. Wilson, "Development of Switchable Polarity Solvent Draw Solutes," International Forward Osmosis Association (IFOA) World Summit, Vancouver, Canada, September 2015 (invited).

Wilson, A. D, "Design and Function of Switchable Polarity Solvent (SPS) Draw Solutes," INL Early Career Research Symposium, July 2015.

Wilson, A. and C. Orme, "Further Studies of Switchable Polarity Solvent (SPS) as Draw Solutes for Forward Osmosis," North American Membrane Society (NAMS) 24th Annual Meeting, Houston, Texas, June 2014.

Wilson, A. D., "SPS FO Water Treatment Technology," Emerging Tech Accelerator Water Reuse Innovation Showcase, Web, July 2015 (SPS FO technology was one of two next-generation water-treatment technologies that was invited to be presented to the 266 attendees representing 199 unique commercial entities).

14-080—Battery Material Characterization Technologies

Dennis C. Kunerth

The development of advanced battery technologies requires the development of improved materials, material diagnostic tools, and methodologies to monitor battery components in operando. The use of nondestructive evaluation (NDE) methods such as ultrasonics, eddy currents, or thermal wave imaging for use with battery materials, geometries, and service environments provide one route to obtaining vital information relevant to materials and device performance. NDE methods were investigated to characterize battery materials and to study the dynamics of in-service battery component degradation, thereby developing INL's capability to support battery materials R&D.

The technical objectives of the proposed research were three fold: (a) determine feasibility via laboratory testing of selected NDE methods to detect and/or monitor, in real time, battery material parameters such as porosity (Year 1); (b) develop diagnostic tools based on viable NDE methodologies into laboratory-based battery material R&D capabilities (Years 2 and 3); and (c) evaluate the viability of using the NDE methodologies for in-service battery diagnostics and management (Year 3).

Most battery and battery-material characterization procedures use either expensive techniques or are performed in a destructive manner. The use of NDE provides a cost-effective means to understand battery performance and to more quickly understand changes that occur within the battery. Identification of physical processes provides systems models that can be used to estimate the state of battery health to better approximate the actual conditions within the battery. NDE approaches have been used to characterize battery materials but were primarily limited to neutron/x-ray radiography and neutron diffraction. To date, only one reference on the use of eddy currents to measure the state of charge in nickel batteries via an electrode impedance method has been found.[1] However, that article noted that the "artifacts" associated with the impedance measurements may provide a means to detect electrode degradation. This insight provides perspective on the novelty and significance of the proposed approach.

Summary

The Year 1 objective of this LDRD was to determine the feasibility, via laboratory testing, of selected NDE methods to detect and/or monitor, in real time, a battery material parameter such as porosity. Ultrasonic, eddy-current, and thermal-based techniques were evaluated. Year 1 results are provided in the FY 2014 LDRD annual report (Project Number 14-080).[2]

Due to the nature of the commercial 2032 battery button cell construction initially evaluated, the material variation responses could not be specifically tied to a single physical material change in the battery. To correlate eddy current responses to battery material variations, an alternate battery configuration better suited for experimentation was selected. Spinel lithium nickel manganese oxide (LNMO) half-cell test samples were fabricated, and charge/discharge cycles were performed with eddy-current monitoring. Figure 1 is the recorded eddy-current response for a charge/discharge test. Plotted are the two eddy current signal components with time.

The ability to use eddy currents and electrochemical signals to jointly probe a battery during cycling allows a more complete set of information to be obtained. The primary focus of early work for this project was to investigate the ability to obtain both sets of data in a parallel manner. During testing, no change in the open-circuit voltage of a spinel LNMO-based half-cell was observed, signifying that the eddy currents were not perturbing the system. However, upon the application of a constant current to the LNMO half-cell, distinct signatures in the

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[1] Mancier, V., et al., "A Contact-less Method to Evaluate the State of Charge of Nickel Batteries Using Foucault's Eddy Currents," *Journal of Power Sources*, Vol. 117, Issue 1-2, May 15, 2003, pp. 223–232.

[2] D. Tomchak and H. Rohrbaugh, *INL Annual Report FY 2014 LDRD Project Summaries*, INL/EXT-14-33589, February 2015.

eddy-current signal were observed that correlated with transitions that occurred within the electrode material (Figure 2). Follow-on work found that changes in temperature can be clearly observed using the combined methods. This is significant because eddy-current analysis using different frequencies can alter the depth of the battery being investigated. As such, heat information that is more directly related to the area of generation could become available. These data would be a significant improvement over following the skin temperature of a cell, as is currently done, and would enable more advanced understanding of material performance and degradation.

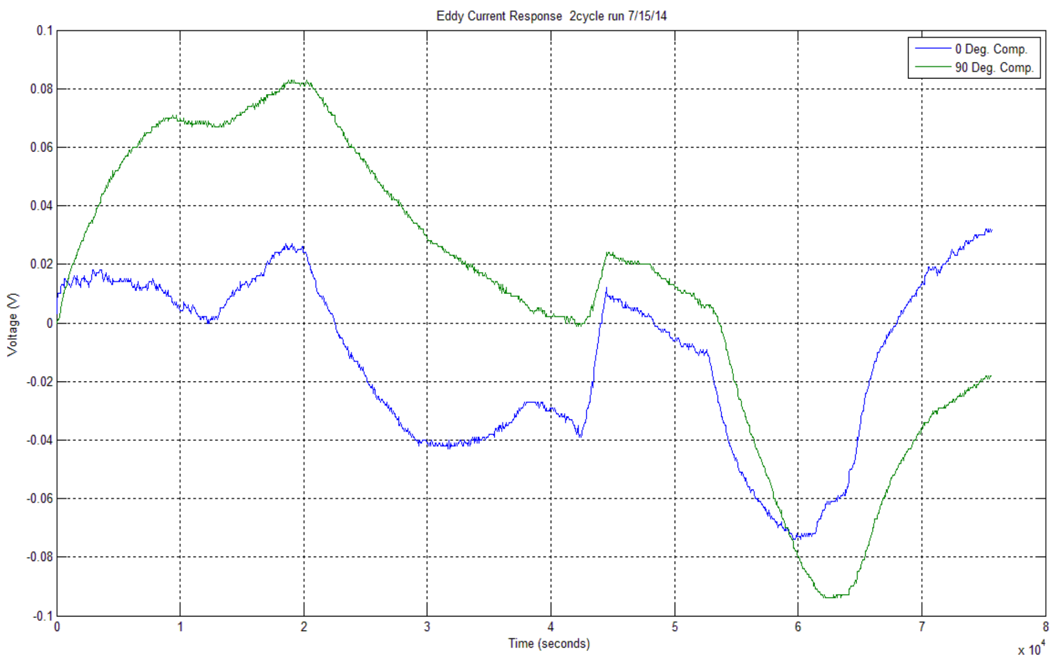

Figure 1. Eddy-current response to charge/discharge cycles in a Spinel LNMO half-cell.

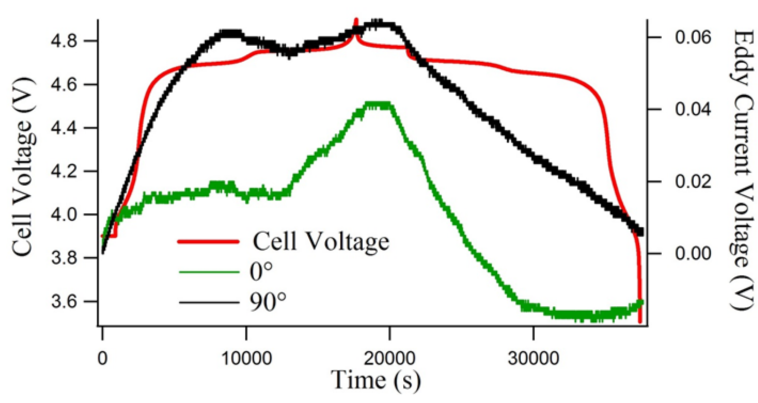

Figure 2. Correlation of eddy-current response to material changes in LNMO half-cell.

To better understand the role of temperature, a route to control temperature using a copper block fed with a controlled-temperature liquid feed was designed. Using this experimental scheme, it was possible to remove the impact of external fluctuations from the measurement. Doing so proved to decrease the variability in signal and provided a solid link between eddy-current response and voltage profile, as shown in Figure 3. Of note is the direct correspondence between changes in voltage profile that occur in the 4.6- to 4.75-V range in both the charge and discharge profiles, which also show up in both the 0- and 90-degree composite eddy-current profiles. This change can be tied to the $Ni^{2+/4+}$ redox couple in the cathode material. Also of note is that the eddy current response does not directly correlate with voltage during early portions of the charge cycle and the later stages of the discharge cycle, meaning that secondary information not directly attainable from the electrochemical response is provided by monitoring the eddy current.

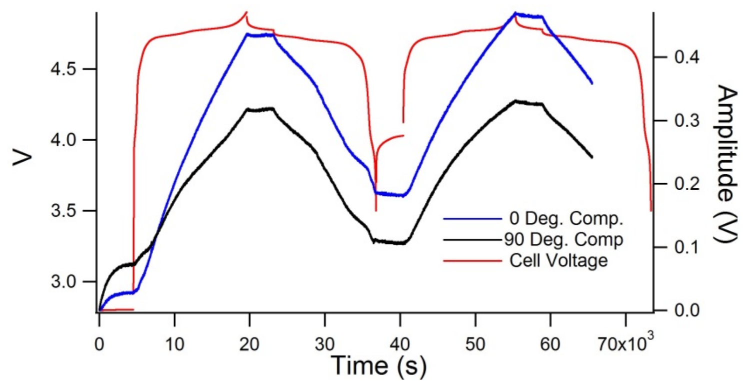

Figure 3. Voltage and eddy-current response for an LNMO/lithium half-cell cycled to 4.9 V at a C/10 rate.

Benefits to DOE

The goal of this LDRD is to develop R&D diagnostic tools and health-monitoring sensor technologies that will facilitate the development of advanced, energy-efficient battery technologies. This fits within the mission of the DOE Office of Energy Efficiency and Renewable Energy. Its mission is to accelerate the development and facilitate the deployment of energy-efficiency and renewable-energy technologies and market-based solutions that strengthen U.S. energy security, environmental quality, and economic vitality.

14-086—Development of a Microgrid/Smart Grid Test Bed for ESL and Super Lab Initiative, with Load Variability Characterization and Control for Renewable Energy Integration

Kurt Myers, Jason Bush, Jake Gentle, Bob Turk, Porter Hill, Manish Mohanpurkar, and Rob Hovsapian

With increasing integration of renewable energy sources into existing power-delivery systems, the ability of the legacy grid and market structures to accommodate these sources will be exceeded rapidly. The ability to understand, test, and model the system dynamics of real-world microgrids and distributed energy resources (DERs) at multiple scales and geographic locations is essential to successfully increasing the penetration of renewable energy sources into existing grids and markets. The developing micro/smart grid platform at INL aims to address these issues through DER grid and microgrid testing, controls research, and modeling in an integrated, collaborative environment. To achieve this goal, INL is designing and constructing an open-source smart grid platform with integrated control systems and component interaction R&D; developing scalable grid models from acquired data; integrating and testing high penetration levels of inverter-based renewable energy generation, battery storage, and load control; and working with industry to begin hardware and software integration testing for future microgrid and DER applications. Additionally, this platform is allowing direct testing and demonstration of various topologies of hardware (including smart inverters or other power electronics systems); electrical, mechanical, and controls interactions; and grid-type energy storage, all of which would be difficult or impossible to accurately simulate when fully coupled to a larger microgrid or full utility grid system. One novelty of this research is its aim to determine the contribution of variability from renewable generation and various load types, and how management, regulation, and control of grid systems can benefit through optimized integration and improved use testing of new and existing load, storage, and generation resource technologies.

This work is providing INL with a state-of-the-art test bed for analyzing the dynamic, combined behavior of renewable generation, energy storage, traditional generation, and load. Furthermore, the research into controllers for energy and storage management schemes that provide user/grid security, cybersecurity, and enhanced grid economics will develop state-of-the-art capabilities/intellectual property that can be shown as low-cost resources within well-designed electricity markets or microgrids.

Summary

Significant improvements are needed to control and manage power systems (both large grids and microgrids) that have increasing levels of variable generation and energy storage systems (ESSs). (There is also a need to better define and achieve acceptable levels of technical and economic performance, as well as system complexity.) In addition, stable control of systems with at least 50% average renewable energy content continues to be a challenge both technically and economically. And expected use impact to ESS performance, aging, and life-cycle costs need to be quantified.

To meet these challenges, the goals of this project include researching and developing a more neutral (R&D-based), two- to three-level microgrid control system and architecture (with manageable complexity), including inverter control modifications (if experiments show that to be necessary). R&D to achieve this will utilize associated test-bed and monitoring systems with control-modified voltage and current-source (alternating-current [AC]-coupled) inverters, ESS (secondary-use lithium-ion, flow, and other battery options), and variable generation/loads. The project will also include use-case measurement and experimentation with secondary-use and other ESS systems and will develop diagnostic and prognostic findings and needs for continuing R&D in conjunction with other energy storage expertise.

In FY 2015, baseline testing and use-case experimentation with the battery storage systems began, with one of the secondary-use lithium-ion systems performing as anticipated so far. Another lithium-ion pack encountered issues early in the process and was removed from the system. Future energy storage options for R&D are in development (other secondary-use and new flow batteries), but baseline findings further demonstrate the need for continued analyses, testing, and standards development for use-case and life-cycle/cost implications of ESSs used in power grid and microgrid systems. Initial testing of a lithium-ion truck battery indicates a remaining energy capacity of 71 kWh (the capacity was 80 kWh when new), and roundtrip efficiency on the AC side is just under 83% in the system when cycling between 90 to 40% and back to 90% state of charge. The expectation is that this battery can perform daily cycling for solar management and peak shaving for up to 10 years with power-level and operational-temperature constraints. Research and collaboration on grid battery use-case impacts on life-cycle/performance continues development.

The first phase of major metering, communications, tracking, and database systems is in place and was completed in FY 2015. Primary-system and component controls have been established and programmed, and transition/stability testing was underway the last few months of FY 2015. System stability and the ability to island away from the main utility grid and reconnect have been established. Modifications have been completed to tighten up the microgrid system frequency and to allow the other grid-tie inverters to stay connected in AC coupling mode to the main grid-forming inverter when in islanded mode. Protective settings are also being assessed and modified, as needed. The secondary level of control R&D is now starting and will be a major focus for continuation and completion in FY 2016. Peak shaving and demand response algorithms are also in development, and experimentation with these will continue into FY 2016. Other progress includes microgrid-electrical and economic-model developments in several software modeling systems, including Homer, EasyPower, SKM, Real-Time Digital Simulator, and PSCAD. The project has also influenced several recent DOE grid modernization and U.S. Department of Defense (DOD) proposals and efforts. The project has also attracted significant industry interest, including collaboration and implementation of OSISoft PI database historian systems for experimental data collection and analytics.

The project, in conjunction with related R&D, has utilized postdoctoral work to establish the first R&D national laboratory-to-laboratory Real-Time Digital Simulator system linkages with DER assets to enable transmission/communication dynamics and controls interaction modeling. It is the first in the Northwest to set up grid-tied and microgrid research testing and characterization for secondary-use electric-vehicle batteries and to enable microgrid storage systems for under $300/kW hour (storage portion only). It has also enabled a pathway for other future grid-scale energy storage R&D at INL and has established collaborative links with cutting-edge energy storage and the smart grid industry. This future grid storage work will likely include exciting flow-battery technologies that have the potential to lower costs and improve life-cycle/use-case abilities into ranges that will allow better safety and widespread adoption. The project has established new research capability in power electronics controls and systems interactions for microgrid-to-grid transitions for systems with high renewable-energy penetration, energy storage, and load control. The project has also begun integration/R&D with controllable electric-vehicle charging systems into a grid R&D environment with the vehicle storage group and other collaborators.

Benefits to DOE

This research supports the DOE goal of solving key technological challenges in making clean energy efficient and affordable while maintaining reliability and resiliency. This project is beneficial to DOE because it is developing smart grid/microgrid and DER integration technologies in addition to testing and modeling assets that will assist others in meeting federal goals for clean energy implementation and integration, as well as grid modernization. DOE is pursuing multiple efforts in DER, energy storage, grid modernization, and renewable energy integration, and this project is positioned to provide research and demonstration avenues across these areas in conjunction with links to utilities, industry, and DOD partnerships and efforts. This work will also benefit the DOD, utilities, industry, and other partners through test and research input into their planning, development, business/economic dispatch, and operational models and processes.

Publications

Bhattarai, B., B. Bak-Jensen, J. Pillai, J. Gentle, and K. Myers, "Overvoltage Mitigation Using Coordinated Control of Demand Response and Grid-tied Photovoltaics," *SusTech 2015, IEEE Conference on Technologies for Sustainability*, Ogden, Utah, July 30–August 1, 2015.

Chanda, S., M. Mohanpurkar, A. K. Srivastava, and R. Hovsapian, "Study of CERTS Microgrid Resilience after V2G Integration," in submission process.

Mohanpurkar, M., R. Hovsapian, et al., Conference paper on capability improvement for integration of Real-Time Digital Simulator with communication network simulation, and NREL co-simulation, in preparation.

Presentations

"Metering for Power Systems and Microgrid Planning," Poster Presentation, AWEA Windpower 2015, Orlando, Florida, May 18–21, 2015.

"Use of Wind Energy in INL and Other Microgrid Systems," Poster Presentation, AWEA Windpower 2015, Orlando, Florida, May 18–21, 2015.

"Renewable Energy/Power Systems Development and Integration: Testing and Use-Case Experiences for Grid-Tied/Micro/Island Grid Applications of Battery Energy Storage," The Battery Show 2015 Conference, September 15–17, 2015.

"Renewable Energy Development and Integration, Microgrids, ESS and Power Systems," NWPPA Power Supply Conference.

14-091—Battery Health Estimation Based on Self-Discharge Fast Measurement and Soft Short-Circuit Detection

Sergiy Sazhin, Eric Dufek, Kevin Gering, and John Morrison[1]

Battery energy storage is destined to occupy a significant segment of our domestic energy strategy because it impacts electric-drive vehicles (EDVs), grid and microgrid storage, and a growing number of consumer applications. Lithium-ion cell chemistries are at the forefront of providing high-density energy storage. However, lithium-ion batteries employ flammable components and may have unpredictable catastrophic failures (CFs). One of the root causes of CF is an imbalance among the cells in the battery pack due to increased self-discharge (SD) in some of the cells and/or the formation of shorts within cells that subsequently elevate SD. Conventional methods to measure SD are time-intensive (days), costly, insensitive to soft (nascent) short-circuit detection, and therefore infeasible for onboard applications.

This project aims to develop a new method for determining SD occurrences and incorporating the SD sensing metric (as a root-cause critical parameter) in advanced battery management systems (BMSs) for EDVs and stationary energy-storage applications (e.g., the grid market). This research also aims to develop a faster method, with high accuracy and sensitivity to soft shorts detection and with clear distinction from prior R&D efforts.

Summary

During FY 2014 (Year 1) and FY 2015 (Year 2), several experimental and modeling variations of a new method were examined. The challenges were very small, noisy, and sometimes unreproducible signals, as well as long measurement times (more than12 hours in the initial preproposal approach and days for conventional measurement). Reproducibility was improved by keeping the measurement device at stable temperature. Other challenges were met with faster-than-anticipated test procedures that allow SD measurements in 1.5 hours or less, with predictions of SD values at different temperatures and battery charges. This prediction capability is essential for prognostic scenarios of battery performance. A significant decrease in the time of the measurement and prediction of SD values was achieved by synergistically combining modeling with experimental approaches. The new modeling approach allows using partial initial data sets to predict SD value with no need to run the measurement for extended periods of time. The modeling was validated with overall average deviation between experimental data and model values around 6% (see Figure 1). For detection of battery short-circuits, the method was successfully validated on the cells with artificially applied external shorts of different severity. Ultimately, the work has resulted in a U.S. patent application on the combined approach and a journal manuscript for submission to the *Journal of Power Sources* pending the patent application filing. The work was presented on several internal LDRD reviews. Tasks in FY 2016 (Year 3) are intended to develop more

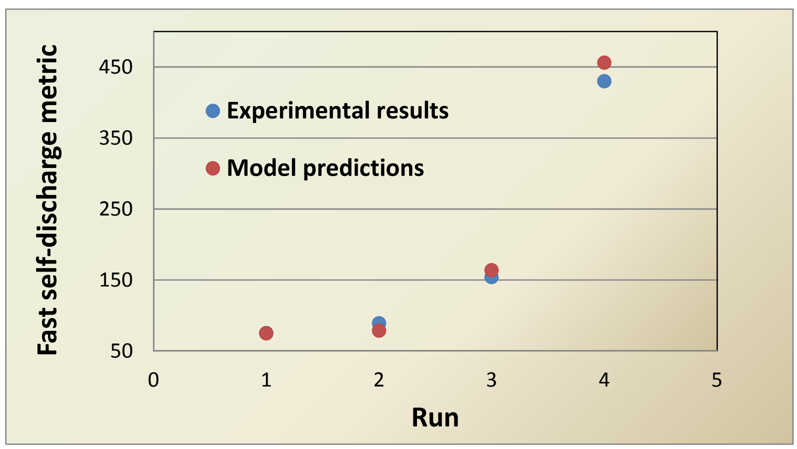

Figure 1. Comparison of experimental and model values for the fast self-discharge metric.

[1] Montana Tech of the University of Montana

rigorous technical data and provide multilevel validation to gain recognition for the utility of the method in a diverse range of industry applications. Follow-on publications and presentations are anticipated.

The main research findings are as follows. Contrary to known methods for the measurement of SD, the method developed under this LDRD allows an accurate extraction of a pure SD metric under controlled conditions. The newly developed metric occurs when all other processes running in parallel in the battery are ceased. SD is a nonlinear function of time; therefore, the developed fast method to economically measure actual in-time SD values is beneficial. This is especially essential for the detection of intermittent soft (nascent) shorts, which have the potential to lead to CF. The method is noninvasive, chemistry agnostic, compatible with existing BMSs, and capable of detecting nascent internal shorts far before the point at which a CF may occur.

The potential impact of this technology is reduction/prevention of battery-related accidents, enhanced system performance (diagnostic and prognostic), reduced manufacturing and battery maintenance cost by identifying faulty cells, and overall improved consumer confidence.

Benefits to DOE

The technical relevance and novelty of the work lies in a completely new capability to monitor the state of battery health on a regular basis with the ability to detect early battery malfunction, prevent CFs, and predict battery life at different application scenarios. The current state of the art does not allow this. The research performed during FYs 2014 and 2015 provides a solid basis for future success of the project and method.

The identification and early detection of battery short-circuits benefits several DOE missions. The energy and national security missions will benefit through the elimination of CF events and the cost-effective increase in battery life. This will promote the penetration of lithium-ion batteries into the EDV and grid markets and will reduce anxiety among battery end users. Electrification of U.S. vehicles and increased battery-based energy storage will lead to less demand for foreign energy sources, providing enhanced national security. CFs are generally very harmful for the environment and costly to cleanup. Therefore, the enviromental quality mission will benefit through elimination of battery failures, and increased performance of energy storage systems will lead to an overall increase in energy efficiency and a reduced need for fossil-fuel energy, thus reducing the generation of greenhouse gases. The science and technology mission will benefit through advanced diagnostic methods for energy-storage applications that will aid in advancing the mechanistic-level scientific understanding of processes occurring in battery system architectures. This work also falls within the mission of the National Highway Traffic and Safety Administration within the U.S. Department of Transportation. Additionally, branches within the U.S. Department of Defense would certainly benefit from this capability applied to unmounted soldier applications, submarines, and critical forward-command energy-storage scenarios.

Publications

Gering, K. L., S. V. Sazhin, and E. J. Dufek, “Battery health estimation based on self-discharge fast measurement and detection of shorts. Part II. Modeling approach,” *Journal of Power Sources*, publication planned for FY 2016.

Sazhin, S. V., E. J. Dufek, and K. L. Gering, “Battery health estimation based on self-discharge fast measurement and detection of shorts. Part I. Experimental approach,” *Journal of Power Sources*, manuscript to be submitted pending patent application filing.

Sazhin, S. V., E. J. Dufek, and K. L. Gering. “Battery health estimation based on self-discharge fast measurement and detection of shorts. Part III. Validation for soft short-circuits detection,” *Journal of Power Sources*, publication planned for FY 2016.

Patent Applications

Sazhin, S. V., E. J. Dufek, and K. L. Gering, Systems and Related Methods for Determining Self-discharge and Internal Shorts in Energy Storage Cells, under finalization at patent firm.

14-095—In Situ Measurement of Electrolyte Chemistry in Battery Cells during Operation

Gary S. Groenewold, David Jamison, Cathy Rae, Kristyn Johnson, Chris A. Zarzana, and Kevin Gering

Lithium-ion batteries are remarkable power storage devices capable of delivering power over repeated discharge/recharge cycles and a range of environmental conditions. Nevertheless, lithium-ion battery performance is eventually degraded as a result of chemical and physical changes within the cells. If time- and use-dependent behavior were known, it is likely that informed approaches to mitigate deterioration and improve performance would emerge. Unfortunately, battery cells are sealed to prevent reaction with the ambient atmosphere, so it is difficult to measure quantitative chemical changes occurring within the cell. The objective of this research is to develop lithium-ion battery cells that will enable chemical interrogation in the form of sub-microliter sampling and analysis, and in situ vibrational spectroscopy, without compromising the integrity or function of the cell as it undergoes discharge/recharge cycling. It is hypothesized that diagnostic changes in the chemical composition of the electrolyte mixtures can be measured as the battery ages and progresses toward eventual failure.

Achieving this objective is challenging because the total quantity of electrolyte present in a typical cell is small. However, the project leverages the recent development of mass spectrometry analysis strategies that require only a small fraction of a microliter, so a salient challenge is to manufacture a cell with ports that support periodic sample collection.

Summary

The approach adopted for cell fabrication has been to design pouch cells for use in a chemical-characterization test bed. In fact, coin cells were originally considered based on their widespread application. However, coin cells have exceedingly small volumes and steel walls that cannot be easily penetrated. The pouch-cell design that was adopted at the end of FY 2014 circumvents these impediments and contains identical chemistry. The pouch cells employ an aluminized polymer housing that can be easily fitted with a sampling port (Figure 1) or with a port that holds a miniature infrared probe used for making vibrational spectroscopy. The initial prototypes displayed reproducible discharge/recharge cycling from $V_{max} = 4.7$ to $V_{min} = 2.7$, so a production run was initiated to manufacture 15 cells for an experimental campaign that would evaluate cell performance (a) with and without the sampling valves, (b) operated at 30 and 50°C, and (c) operated with and without a fire-retardant compound added to reduce flammability and improve cycling reproducibility.

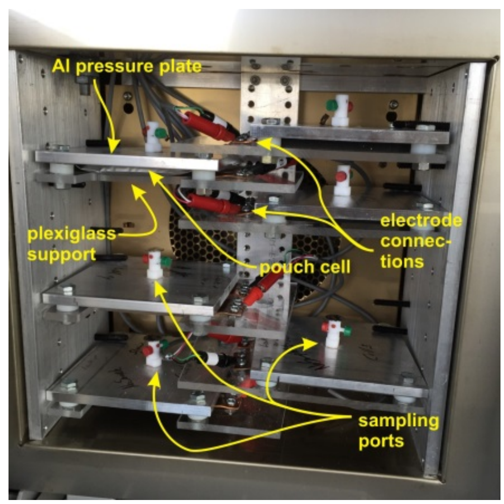

Figure 1. Six pouch cells (fitted with sampling ports) situated in a test oven.

The initial production run was slowed by premature cell failures, which were initially caused by leaking seals in the pouch polymer and cathode delamination. Modification of the thermal sealing procedure and cathode adhesive solved these problems. Later cell failures were attributed to voltage cycling too close to the V_{max} and V_{min} levels, which has led to a change in the test plan. As of September 2015, a total of eight cells were being cycled in temperature-controlled chambers made from gas-chromatograph ovens.

A gas-chromatography/mass-spectrometry approach was adopted for measuring the relative concentrations of the electrolyte components. Dilution of a sub-microliter sample by >5 orders of magnitude resulted in analytical signals that were at the upper end of the instrumental linearity response. Analysis of head space was also demonstrated, and this is likely to be the best path forward: exposure of a solid-phase microextraction tip to the residual vapor in the microsampling valve also produced abundant signal. In addition to detecting the carbonate electrolytes, degradation impurities were also seen; this was significant because it showed that indicators of solvent breakdown could be detected and suggested mechanistic pathways, specifically ester hydrolysis. Surprisingly, electrospray ionization mass spectrometry did not work well for the carbonate analysis, but the technique was excellent for analysis of the fire-retardant additives. These phosphazene ring compounds have anywhere from one to four trifluoromethyl groups, all of which were readily measured using a submicroliter sample. The measurements also revealed the affinity of the additives for lithium ions, which is a key feature of their function and has only been theoretically calculated so far.

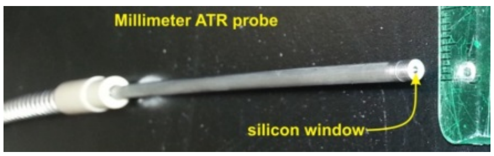

Figure 2. Photograph of the miniature attenuated total reflectance infrared probe.

Attenuated total reflectance infrared spectroscopy provides molecular structure information for the carbonates, and an exceptionally small attenuated total reflectance probe was fabricated in 2015. The diameter of the probe is 3 mm (Figure 2), and an interfacing flange for the pouch cells has been developed. The probe is capped with a silicon window that protects an AgCl-AgBr fiber, which has high transmission over the salient range of infrared frequencies characteristic of the carbonates. Initial measurement tests were under way in September 2015.

Benefits to DOE

This project holds excellent potential for providing a much improved understanding of electrolyte chemistry that impacts battery performance and ultimate lifetime. The range of DOE and government functions that would benefit from improved battery performance would be vast and would include applications in national security, energy storage, and environmental remediation. Consequent improvements in battery technology would have wide-reaching effects benefitting virtually all government agencies.

14-106—Understanding the Growth of Ultra-Long Carbon Nanotubes

Joshua J. Kane and Robert V. Fox

Carbon nanotubes (CNTs) have extraordinary properties, including a tensile strength 100 times greater than steel, a thermal conductivity rivaled only by the purest of diamonds, and an electrical conductivity similar to copper but capable of carrying significantly higher current densities. These properties make it a desirable material for future composites, coatings and films, energy storage, and environmental applications.

Current CNT applications are not able to take full advantage of these unique properties due to the inability to grow aligned arrays of macroscopic-length CNTs. A majority of industrial applications currently use a random dispersion of CNTs within a bulk material to slightly augment the material properties of the composite. The major factor limiting CNT growth is the poisoning and deactivation of the catalyst used. The purpose of this project is to understand the factors affecting the deactivation kinetics at a continuum level. Once the kinetics are understood, a solution can be proposed to prolong growth or potentially eliminate deactivation altogether. Factors such as initial catalyst particle size, catalyst substrate, and the gas composition will be varied to help understand their role in the deactivation kinetics.

Summary

Project achievements in FY 2014 included the design, acquisition, and receipt of an experimental system capable of measuring the rate of carbon accumulation within a chemical vapor deposition chamber. Using this system enabled the development of a synthesis method for the production of iron-oxide nano-catalysts for CNT growth. The catalyst particles were analyzed via atomic force microscopy in the Surface Science Laboratory at Boise State University.

In FY 2015, significant strides have been made toward enabling investigation of the mechanism of CNT growth. The first major milestone in FY 2015 was the optimization of the custom-built chemical vapor deposition reactor for in situ measurements of CNT growth rate. The gas analyzer, a quadrupole mass spectrometer, allows the chemical composition of the outlet gas stream to be measured. Using measured composition and flow rate, the rate of CNT growth can be determined. In situ analysis of CNT growth rate is rare in the CNT literature and sorely needed according to some of the leading experts in CNT growth kinetics.[1] In situ analysis of the CNT growth rate combined with chemical composition information goes well beyond "common/traditional" kinetics experiments and will provide a great deal of insight into the CNT growth mechanism. A significant challenge to completion of this optimization was the consistent and precise control of moisture content to ±5 ppm over a range of 100 to 5,000 ppm moisture with a fast response time to changes and variations in gas flow rates. This was solved with a novel direct moisture-injection system utilizing a high-resolution microfluidic pump rather than a traditional gas bubbler with a temperature-controlled water bath.

The second major milestone was the development of a standard, reproducible method for the growth of ultra-long CNTs to begin testing the influence of the aforementioned factors. Figure 1a shows vertically aligned arrays of CNTs on a 1-inch silicon wafer substrate. The heights of the arrays are just over 1 mm. To date, the largest arrays grown have a height of approximately 2 mm. This is approximately one-fifth the length of the tallest reported CNT arrays in literature. The multilayer substrates used were developed through collaborations with three groups at Boise State University: the Surface Science Laboratory, the Idaho Microfabrication Laboratory, and Elton Graugnard's laboratory.

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[1] Puretzky, A. A., D. B. Geohegan, S. Jesse, I. N. Ivanov, and G. Eres, "In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition," *Applied Physics A*, Vol. 81, pp. 223–240.

Initial CNT characterization of ultra-long, vertically aligned CNTs has included atomic force microscopy, scanning electron microscopy (Figure 1b), energy-dispersive spectroscopy, and x-ray diffraction. Transmission electron microscopy is in progress to assess the quality and type of CNT. Additionally, collaboration with Matteo Pasquali at Rice University is in development to further characterize CNT array quality. Dr. Pasquali is a leading expert in the field of CNTs and has developed considerable expertise in the field of CNT characterization.

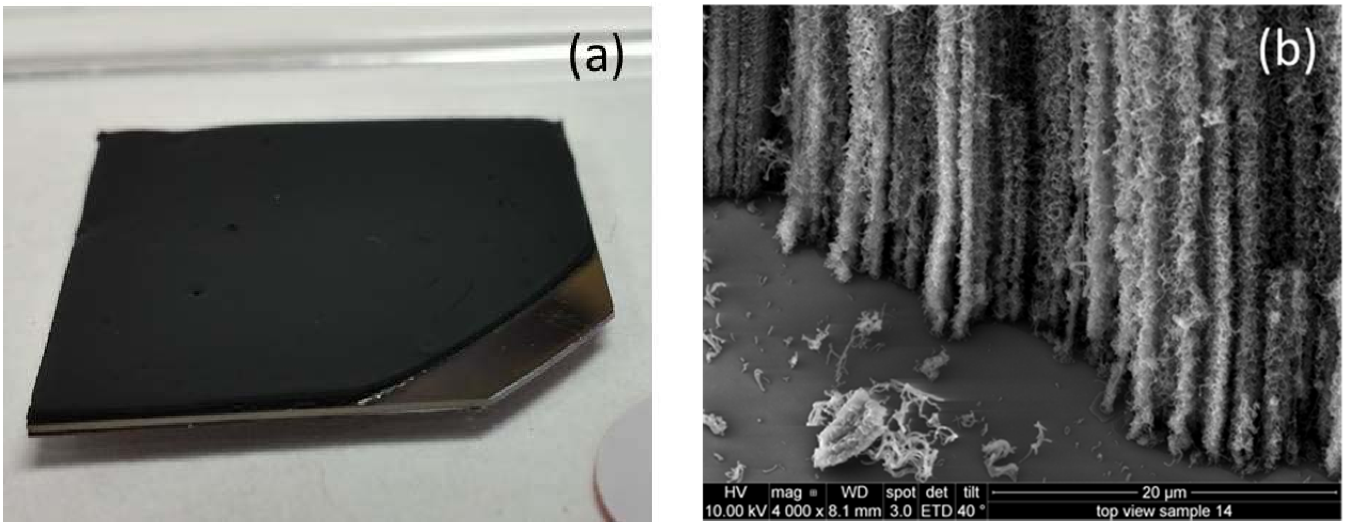

Figure 1. One sample of vertically aligned CNTs grown on a silicon wafer substrate during FY 2015 (a) (the CNT array is just over 1 mm tall) and an electron micrograph of vertically aligned CNTs growing upward from a 1-nm-thick iron film on a silicon wafer (b).

Finally, in addition to accomplishing two major milestones, initial kinetics studies investigating the role of hydrogen gas (H_2) in the production of CNTs from ethylene ($H_2C{=}CH_2$) has shown a direct relation between the amount of H_2 in the reactant gas mixture and the amount of methane (CH_4) produced in the gas phase. Lowering the H_2 concentration in the inlet gas stream decreases the amount of CH_4 produced. CH_4 produced in the gas phase may readily decompose over an iron catalyst used and form an amorphous layer of carbon that can inhibit further adsorption of ethylene and ultimately stop CNT growth. There appears to be no reports of this in CNT literature.

Benefits to DOE

DOE's mission involves the assurance of U.S. security and prosperity through transformative science and technological solutions that address current and future energy, nuclear, and environmental needs. CNTs have numerous materials-based applications relevant to the DOE's mission, including:

1. Lighter-weight electrical cable capable of handling significantly higher current densities than copper
2. High surface area catalyst support for higher product yield catalysts
3. Low-pressure differential filtration systems for removal of biological contaminants
4. Advanced alloys and composites for extreme environments, including nuclear reactors and high-temperature applications
5. Enhanced mechanical stability of membranes for separation of critical materials from waste streams
6. Sensors for extreme environments.

The collection of in situ apparent reaction rates from gas analysis within a reaction vessel is not a novel concept in and of itself. The use of this technique is rarely applied to the growth of CNTs, and most investigations of the kinetics of CNT growth are limited to the measurement of a CNT array height ex situ. The lack of application may in part be due to the number of species involved, the non-trivial mass spectra, or perhaps the difficulty in applying this in situ technique to a gas environment at high temperatures. Regardless, the lack of in situ experimental data has severely limited the CNT research community's ability to interrogate the growth mechanism.[1] Collection of gas composition data in situ allows the growth rate to be determined and provides valuable insight into the role of each component within a CNT reactor's influent gas. This insight advances the CNT state of the art by improving the understanding of the reaction mechanism. Ultimately, this will allow better control over the growth of carbon nanotubes.

15-125—Phosphoranimines for Advanced Battery Applications

Eric J. Dufek, Joshua S. McNally, John R. Klaehn, Harry W. Rollins, and Riley Parrish

Currently, organic carbonates are the principal solvent component in electrolytes for lithium-ion batteries. For low- to medium-voltage use, these compounds are effective, but they suffer at high voltages, and there are questions regarding their safety and long-term stability. In terms of stability, carbonate-based electrolytes begin to degrade at relatively low temperatures, leading to battery performance degradation. Multiple attempts have been made to create electrolytes that maintain performance and increase safety, but none have been fully successful. Falling short of achieving a high level of performance has resulted in an accumulation of new electrolyte chemistries, creating a bottleneck to deployment due to incomplete knowledge of electrolyte blending possibilities and insufficient high-quality validation of performance. Rather than continuing on the current development trajectory, a more streamlined route from chemical discovery to deployment is sought. In that vein, this project has focused on better enabling industry and DOE to advance electrolyte development and deployment by building a "tool set" that is being demonstrated using distinct INL phosphoranimine (PA) electrolyte chemistries. The tool set is composed of two primary components that use a modeling-based architecture to directly link molecule discovery with an experimental framework for performance-level understanding of electrolyte blends.

Summary

In FY 2015, the first year of the project, the aim was to link density functional theory (DFT) models of compounds with synthetic approaches to understand performance changes associated with alteration of the PA chemical structure. The link between DFT and synthesis is to increase the likelihood of creating new compounds that are successful as battery electrolytes. In parallel with the electrolyte development efforts are activities associated with creating better ways to evaluate electrolytes, with a primary focus on electrolyte stability and electrochemical performance.

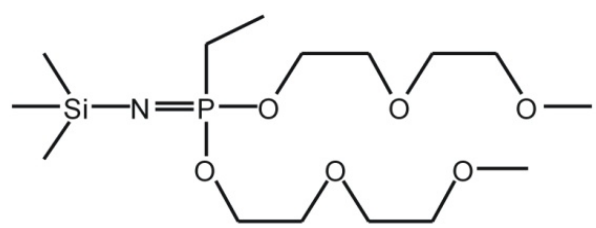

Figure 1. PA-5, a representative PA. The pendants connected to the P are defined as R-groups with the silyl group off the N defined as R'.

Phosphazenes are a class of molecules that contain a phosphorus-nitrogen (P=N) bond as the backbone. As such, they can be oriented in a host of different conformations, including cyclic systems, linear polymeric systems, and monomeric forms. While most research in phosphazenes has been associated with solid materials, distinct subsets of phosphazene compounds exist as fluids, such as oxidatively stable fire-resistant lubricants and hydraulic fluids. Among the many advantages of these P-N-containing compounds are their nonvolatility, nonflammability, thermal robustness, stability at high voltages, and, lastly, compatibility with a host of different electrode chemistries. At INL, research has examined phosphazenes as a co-solvent and at additive levels ranging from 3 to 30% of the solvent volume. While effective at improving the overall safety of lithium-ion battery electrolytes, the cyclotriphosphazenes are limited in the amount that can be loaded into electrolytes without increasing viscosity to a point where performance declines. Rather than continuing on a path that is limited in its overall loading level and by enhanced viscosity, the current work has focused on a newer member of the phosphazene electrolyte family: PAs (Figure 1). As a different class of phosphazenes, PAs are monomeric and have lower molecular weights. This provides a route to reduce viscosity while still providing the adventitious safety aspects of cyclotriphosphazenes.

To date, the project has made technical progress in three primary areas: (a) a synthetic procedure has been developed for the preparation of PA compounds, and a variety of novel PAs, differing in their R and R' groups, have been successfully synthesized; (b) DFT methodology has been developed to provide ab initio models of PAs; and (c) characterization and testing of a PA compound (PA-5, Figure 1) has been carried out, and methods to better understand electrolyte performance in a timely manner have been initiated. As a whole, the project has resulted in two presentations at scientific meetings, three manuscripts are being prepared for submission to publications, and two distinct patent applications have been filed on the work.

Seven PA compounds have been prepared that exhibit differing chemical and physical properties. This exemplifies the ability to tailor PAs to the needs outlined above. All the synthesized compounds have been characterized using ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance spectroscopy.

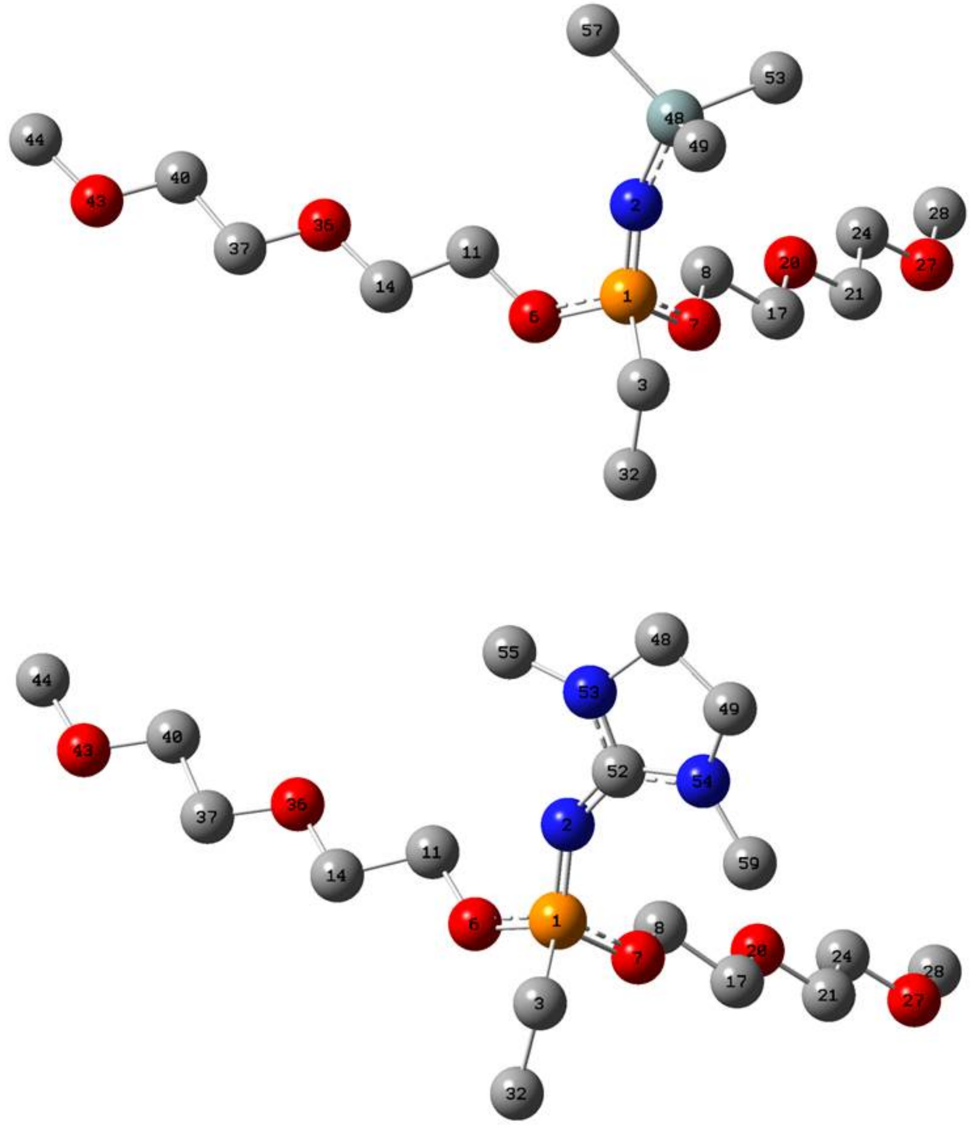

Figure 2. Select DFT model compounds of PA compounds with different R' groups.

In conjunction with the synthetic activities, DFT (Figure 2) has been used to model the seven new compounds and other potential PAs. In line with the focus of the first year of the work, DFT results are now being tied to the physical characteristics of the PA compounds, and potential new compounds are being evaluated using the modeling approach. As a prime example, the computational model configurations have been investigated using DFT to explore the impact of varying substituents on the geometric properties of the compound. In particular, the

P-N-R' bond angle has been observed to change depending on the nature of the substituent bonded to the nitrogen in the PA structure. The change in this bond angle is expected to correlate with the π-bonding character associated with the group and the subsequent character of the bond. This bond angle is hypothesized to serve as an important proxy for the nature of PAs as electrolyte materials. For this reason, DFT has helped guide the synthetic goals of the project.

To help develop a uniform means to evaluate electrolytes, PA-5 has been used as a benchmark compound for the development of a series of validation techniques that can be easily used to study electrolyte behavior for other PA- and non-PA-based systems. These experimental procedures involve electrolyte stability, lithium solubility, conductivity and viscosity measurements, as well as electrochemical testing, including cyclic voltammetry, cycling performance analysis, and cell testing.

As a whole, the activities linking DFT and synthesis of new compounds and the development of means to evaluate electrolytes have been successful in the first year of the project. During continuing work, a more in-depth scientific understanding of the PAs and their role as advanced battery electrolytes will be acquired, and new methods for evaluation will become further refined and more uniform.

Benefits to DOE

Battery manufacturers, DOE, and other government entities such as the U.S. Department of Defense have had significant recent interest in new classes of electrolytes and electrolyte additives that improve the safety and performance of lithium-ion batteries. Improving battery performance is a key concern and a necessity to increase electrification of the U.S. transportation sector. Such a move, which is a key focus of DOE, will decrease demand for foreign energy sources and will reduce carbon emissions. From a military perspective, the interest in safer electrolytes is tied directly keeping soldiers and military assets safe. Recent discussions with members from the automotive and general battery industries have highlighted the need to more thoroughly validate electrolyte chemistries prior to inclusion in the battery manufacturing process. Currently, the deployment process is impeded by the enormous quantity of new electrolyte possibilities and a desire by researchers and inventors to see their contributions succeed. A major focus of the industry interest is on the ability to perform standardized, high-quality validation that is directly tied to performance-driven metrics. The current research provides a novel electrolyte additive that deviates from the purely carbonate-based line of thinking, a research approach that the DOE is interested in. The project is also directly examining metrics and understanding the science of improving battery performance directly in line with the scientific mission of DOE.

Publications

Klaehn, John R., Eric J. Dufek, Harry W. Rollins, and David K. Jamison, "Phosphoranimine-based battery electrolytes," *Journal of Power Sources,* in preparation.

Klaehn, John R., Joshua S. McNally, Harry W. Rollins, Eric J. Dufek, and Arulsamy Navamoney, "Preparation and structural characterization of ionic liquids based on a phosphoranimine backbone," in preparation.

McNally, Joshua S., Harry W. Rollins, John R. Klaehn, and Eric J. Dufek, "Investigation of alkali-ion association with phosphoranimines," *Dalton Transactions*, invited manuscript in preparation.

Presentations

Klaehn, John R., Eric J. Dufek, Joshua S. McNally, and Harry W. Rollins, "Phosphorus-containing electrolytes—expansion to include phosphoranimines for Li-ion batteries," 228th Electrochemical Society Meeting, Phoenix, Arizona, October 15, 2015.

Parrish, Riley, "Electrolyte performance for Na-ion batteries," 2015 Northwest Regional Meeting of the American Chemical Society, Pocatello, Idaho, June 23, 2015.

15-128—Microstructural Evolution and Mesoscale-Coupled Flow-Reaction-Fracturing Processes in Organic-Rich Nanoporous Shales

Hai Huang, Earl Mattson, Travis McLing, Darryl Butt,[1] and Paul Leonard[2]

This project brings together a multi-institutional, interdisciplinary team of computational geoscientists, experimentalists, and material scientists in a focused effort to develop a better understanding of the fundamental physics that controls the behaviors of organic-rich nanoporous shales and the fluids within them. The project coordinates an array of state-of-the-art characterization and imaging tools, including x-ray, scanning electron microscopy (SEM), transmission electron microscopy, and focused ion beam (FIB)-SEM, combined with the nano-indentation test, to characterize and image the evolutions of the microstructures of nanoporous shales in detail and at the highest possible resolution. The computational component of the proposed project—mesoscale models of coupled diffusion-reaction-fracturing processes—aims to develop multiphysics models that will provide physics-based predictions of microstructure evolutions of organic-rich nanoporous shales induced by changes of fluid chemical compositions, temperature, and pore pressure.

Summary

The project was funded and started in late spring (April-May) of 2015. Five months into the project, progress in both experimental and modeling studies, as proposed, includes the following:

- Developed the workflow of using x-ray, FIB/SEM, and transmission electron microscopy to characterize and image the nanostructured shale matrix at different scales
- Applied FIB milling to prepare micropillars, ~5 to 10 μ in diameter, and performed a number of nano-indentation tests, with the objective of understanding the mechanical properties of various components within shale matrix and the nucleation mechanism of microcracks within the shale matrix
- Developed the workflow for conducting molecular dynamics simulations for the organic matter-kerogen embedded in the shale matrix
- Developed a coarse-grained multiphase flow model in pore networks based on the dissipative particle dynamics method, which allows complex pore-scale flow simulations at much larger mesoscale, microns to millimeters, which cannot be reached by classic molecular dynamics simulations
- Developed a grain-scale microgeomechanics model based on a discrete element model, which can be used to predict the deformation and microfracturing of microstructures of shale matrix induced by the swelling stress of kerogen and clay due to adsorption and/or water imbibition.

Figures 1 and 2 illustrate some of the research results obtained during the first five months of the project.

Benefits to DOE

Research into areas such as microstructural changes of nanostructured organic-rich shales coupled with fluid-flow and volume-changing/stress-generating processes such as chemical transformations, swelling/shrinking, sorption/desorption, and thermal expansion/contraction is of strategic importance to the nation's energy security and environmental sustainability. These are basic areas that promise new scientific discoveries with high economic and societal impact. The proposed research has important implications for sustainable and

[1] Boise State University

[2] Pioneer Natural Resources

environmentally friendly recovery of shale gas and oil, geological storage of CO_2 in depleted shales, and underground storage of nuclear waste and other hazardous wastes.

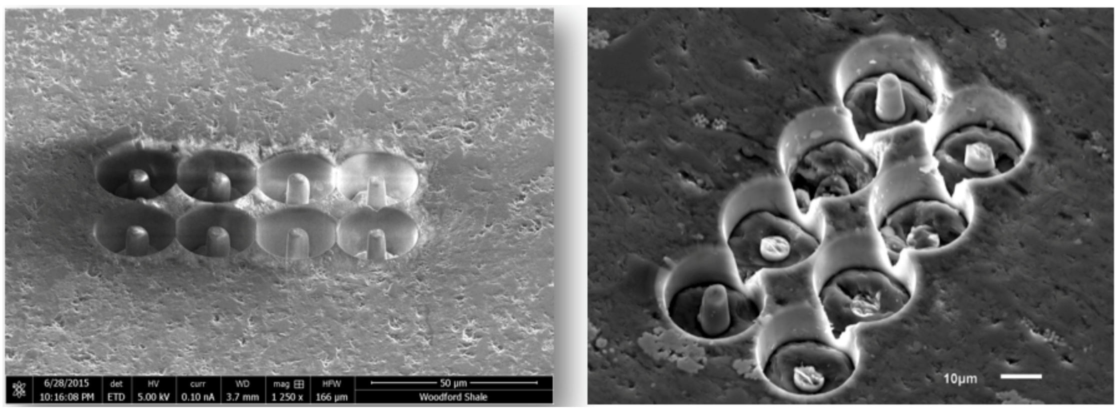

Figure 1. FIB-milled micropillars in a shale sample (left) and the crushed micropillars using nano-indentation.

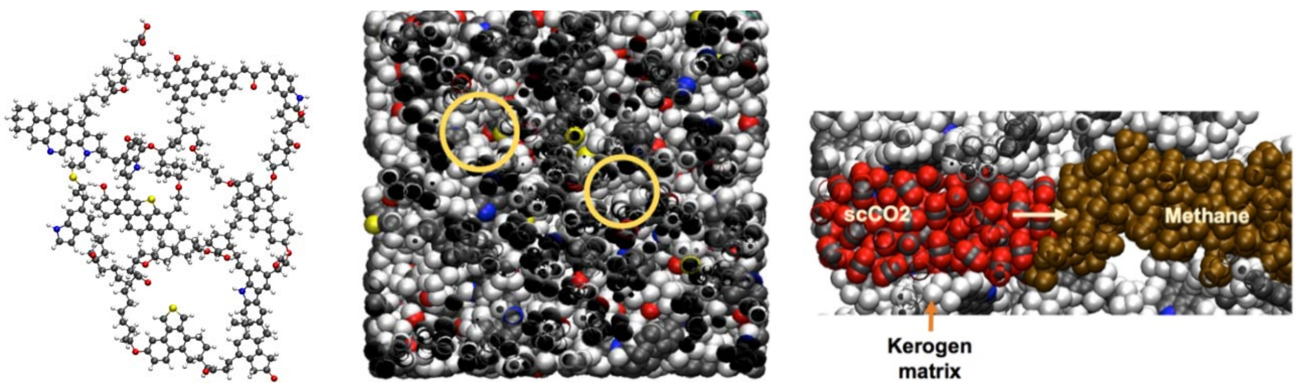

Figure 2. Molecular model for Type-II kerogen (left), a condensed kerogen matrix with sub-nanometer voids (middle), and two-phase flow MD simulations in a nanometer channel with kerogen (right).

Publications

Manas, Pathak, Hai Huang, and Milind Deo, "Carbon Dioxide Sequestration and Hydrocarbons Recovery in the Gas Rich Shales: An Insight from the Molecular Dynamics Simulations," *Carbon Management Technology Conference 2015 (CMTC 2015),* Sugar Land, Texas, November 17–19, 2015, conference abstract accepted.

Pawar, Gorakh, Hai Huang, and Paul Meakin, "Molecular Dynamics Simulation and Sub-nanometer Scale Characterization of Type I, Type II and Type III Kerogen with a General-Purpose DREIDING Force-Field," *Energy and Fuels*, ready for submission.

Pawar, Gorakh, Hai Huang, Paul Meakin, and Ilija Miskovic, "Shifting Paradigm: Understanding the Supercritical CO_2-Enabled Hydrocarbon Recovery in Realistic Sub-Nanometer Organic-Rich Shale Pores Having Different Thermal Maturity Levels," *Carbon Management Technology Conference 2015 (CMTC 2015),* Sugar Land, Texas, November 17–19, 2015, conference abstract accepted.

Xia, Y., H. Huang, and P. Meakin, "A Mesoscale Modeling and Simulation of Multi-fluid Flow in Nano Pores with Dissipative Particle Dynamics," *Physical of Fluids*, ready for submission.

15-135—Dynamic Simulations for Large-Scale Electric Power Networks in a Real-Time Environment Using Multiple RTDS

Rob Hovsapian, Manish Mohanpurkar, and Siddharth Suryanarayanan

This project aims to develop capabilities for geographically distributed real-time simulation using real-time simulators and interconnectivity between different locations. This connectivity will be used to conduct dynamic and transient analysis of large-scale power and energy systems. The other purpose of the project is to address the existing gaps for modeling and simulation of newer devices such as power converters operating in a seconds to minutes time scale. Challenges in predicting transients (nanoseconds to seconds) under increasing penetration of hybrid energy systems that consist of distributed and renewable sources, at the regional and national level, will also be addressed using the research work. The proposed development of these capabilities will foster stronger ties and collaboration with researchers and scientists from other national laboratories, academic researchers, and utilities for future dynamics and transient simulation research for large power and energy systems.

Once the project is successful, the expected outcomes and innovation are as follows:

1. Local or geographically distributed real-time simulation using power hardware in the loop and controller hardware in the loop
2. Electrical/thermal/mechanical subsystem co-simulation at different computational time steps
3. Ways to address data latencies
4. Development of power-grid network equivalence techniques on geographically distributed test systems.

Summary

The research under the scope of this LDRD-funded project is progressing satisfactorily. A data communication link between INL and a partner laboratory, the National Renewable Energy Laboratory (NREL), was established and tested successfully. Distributed real-time power system simulation between Real-Time Digital Simulators (RTDSs) at INL and NREL was demonstrated with very low data latency (~15 milliseconds). In summary:

1. Real-time distributed simulation between INL and NREL was successfully demonstrated in June 2015[1]
2. A linear prediction-based approach was developed for data latency mitigation in July 2015
3. RTDS and the dynamic concentrated solar power thermal model were successfully integrated in December 2014.

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[1] Press articles about INL-NREL demonstration:

1. Science News
   http://esciencenews.com/sources/physorg/2015/05/05/inl.and.nrel.demonstrate.power.grid.simulation.a.distance
2. Phys.org
   http://phys.org/news/2015-05-inl-nrel-power-grid-simulation.html
3. SmartGrid News
   http://www.smartgridnews.com/story/nrel-and-inl-connect-power-grid-technology-over-internet/2015-05-06
4. Worldofrenewables
   http://worldofrenewables.net/inl-and-nrel-demonstrate-power-grid-simulation-at-a-distance/
5. ExecutiveGov
   http://www.executivegov.com/2015/05/energy-department-demos-inter-lab-power-grid-simulations/
6. The Business of Federal Technology
   http://fcw.com/articles/2015/05/06/news-in-brief-may-6.aspx

Dynamic models were developed in RSCAD based on Institute of Electrical and Electronics Engineers standards for transmission and distribution systems. Interfacing of a concentrated solar power dynamic model in MATLAB was done with RSCAD electrical models, and co-simulation was demonstrated successfully. Communication layer data latency mitigation techniques are under development. A linear prediction/correction engine was developed for distributed real-time simulations.

Benefits to DOE

The capabilities developed by this LDRD have helped INL win two projects:

1. California Energy Commission's Red Cross Evacuation Route Microgrid ($400K)
2. Dynamic Modeling and Validation of Electrolyzers to Demonstrate its Value in a Real-Time Environment ($2.1M).

The work and progress in the both of the abovementioned projects are tracked separately from the LDRD work. The LDRD research enables the infrastructure necessary to make progress in the two projects mentioned above.

Publications

Liu, R., M. Mohanpurkar, M. Panwar, R. Hovsapian, and A. Srivastava, "Role of Linear Prediction in Geographically Distributed Real-Time Simulations," in preparation.

Panwar, M., S. Suryanarayanan, and R. Hovsapian, "An MCDA-based Approach for Dispatch of Electric Microgrids," to be submitted.

Presentations

Hovsapian, R., "Laboratory of the Future," for the project Dynamic Modeling and Validation of Electrolyzers in Real-Time Grid Simulation, Demonstration during Dr. David Danielson's INL visit, Idaho Falls, Idaho, June 30, 2015, available online at https://vimeo.com/131928051.

Hovsapian, R., "LDRD Review," Battelle Energy Alliance Board of Science and Technology Committee Meeting, Idaho Falls, Idaho, July 21, 2015.

Hovsapian, R., "DRTS-DRTS Link for Distributed Real-time Simulation," Aalborg 2015 Symposium on Microgrids, Aalborg, Denmark, August 27–28, 2015.

Hovsapian, R., "Dynamic Simulations for Large-scale Electric Power Networks in a Real-time Environment Using Multiple RTDSs," DOE-NE Review during Germantown Meeting, September 22, 2015

Mohanpurkar, M., "Distributed Real-Time Simulations Using RTDS®," RTDS User General Meeting, San Francisco, California, May 5–7, 2015.

Panwar, M., S. Suryanarayanan, and R. Hovsapian, "Performance Metrics-Based Design and Dispatch for Electric Microgrids," Poster Presentation, IEEE Power and Energy Society General Meeting 2015, Denver, Colorado, July 25–30, 2015.

15-140—Expanding the Utility of Advanced Chemical Physics Models for Electrolytes

Kevin L. Gering, Joshua S. McNally, Jianguo Yu, and Eric J. Dufek

Electrolytes play a central role in the performance, safety, cost, and life of the systems they reside in (batteries, refrigerators, water treatment plants, metabolic systems, etc.). For example, electrochemical energy storage devices (such as lithium-ion and sodium-ion cells) are electrolyte-centric and comprise a multibillion dollar market that is projected to have greater-than-linear growth in coming decades to surpass $20 billion per annum. Consequently, a great deal of time and money are spent to obtain laboratory data sets that cover the foremost metrics needed for electrolyte evaluation and optimization. This collective emphasis calls for computational tools that can economically accelerate selection and characterization of advanced electrolyte systems.

To meet this need, a breakthrough computing architecture known as the Advanced Electrolyte Model (AEM) was developed at INL. AEM achieves both speed and accuracy in rendering genome-level information on electrolyte systems. This project seeks to expand the utility of the AEM by coupling it with up-front ab initio techniques such as density functional theory (DFT) and molecular dynamics (MD) that would provide reliable initial estimates of key molecular-scale interactions involving configurational and kinetic metrics. Such a coupling of modeling methods will open, new avenues for applying a unique INL capability to support competitive research in areas of interest to INL, DOE, the U.S. Department of Defense, academia, and the private sector. Both bulk and in situ electrolyte behavior will be studied with the AEM/DFT package because it is well known that interfacial processes can dominate system performance such as in batteries. Over the 1.5-year project, the modeling capability will be applied to existing INL targets that have commercialization impact to accelerate acquisition and expansion of technology territory for INL. The enhanced AEM tool will also be used to gain competitive advantage in proposals.

Summary

The project was funded for nearly six months in Year 1 (FY 2015). During that time, early success was had in identifying molecular metrics and cross-talk methods between AEM and the other computational tools. Successes included expanding the AEM compound library to include INL-invented solvents and other materials that enhance collaboration between INL and Boise State University. To summarize:

1. New compounds were added to the AEM library to support collaboration with Boise State University (Claire Xiong) and other INL principle investigators (Eric Dufek and John Klaehn). Early validation confirmed the accuracy of AEM with the following compounds:
    - Salts for sodium-ion battery electrolytes: $NaPF_6$, $NaClO_4$, $NaBF_4$, and NaTFSI
    - Solvents of interest: DEGDME and TEGDME
    - INL phosphazene solvents for battery electrolytes: FM2, SM4, and PA5.
2. Standardized methods and metrics from DFT and MD were standardized to obtain cross-talk with AEM in terms of two key parameters for electrolytes:
    - *Solvent-to-ion configuration/orientation*. DFT studies have been focused on calculating the ligand-wise bond enthalpies for commonly used organic carbonate solvents and lithium ions. These bond enthalpies are considered representative values that describe the suitability of a chosen ab initio model as accurately representing the binding interaction between Li+ and one or more carbonate ligands. All geometry optimizations and vibrational frequency calculations were carried out using Gaussian 03 (Revision C.02). The B3LYP functional, which uses Becke's three-parameter exchange functional (B3) and the correlation function of Lee, Yang, and Parr was used in combination with the valance triple-ζ 6-311++G(d,p) basis set, which includes polarization functions on all atoms and diffuse functions on non-hydrogen atoms. In

addition, the 3-21G and 6-311G basis sets were used, which do not include any polarization or diffuse functions. All methods found a trend where the ligand-wise bond enthalpies decreased as the coordination number increased, up to a four-coordinate structure, based on energy-minimized geometries.

- *Average solvent residence time around ions* (MD metadynamics). This approach will bridge the gap between conventional MD simulations (picosecond events with femtosecond time steps) and ion-solvation phenomena times (nanosecond events that might require several net nanoseconds per MD run to provide suitable averaging). Metadynamics is a powerful technique for enhancing/accelerating sampling within MD simulations through a history-dependent bias potential and reconstructing the free-energy surface as a function of a few selected geometric parameters called collective variables. The collective variables of metadynamics are related to bond lengths in the defined system.

3. Material was assembled for two papers, with emphasis on lithium- and sodium-ion systems: (a) predicting electrolyte conductivity and (b) predicting solvent-to-ion association and binding energies.

The approach for FY 2016 remains much the same as proposed (allowing for delay of the Year 1 start), with the following goals:

- Finalize a computational “handshake” between DFT/MD and AEM
- Develop interfacial processes involving battery electrolytes with INL phosphazenes
- Understand low-temperature phenomena of electrolytes in porous regions
- Understand switchable polarity solvent behavior and related physical properties across membranes.

Benefits to DOE

The outcome of this work will bring higher confidence and rigor to the design and characterization of advanced electrolytes and related materials for batteries. This work has application to electrical-grid and other stand-alone battery energy-storage systems and aligns with mission areas of the DOE Office of Electricity Delivery and Energy Reliability. Other potential contributions exist within electrified-vehicle battery development under the DOE Vehicle Technologies Program and DOE programs tied to the private sector. Collectively, the success of this project will enhance U.S. domestic energy security (with a related decrease in fossil fuel use) through battery R&D that is accelerated and centered on state-of-the-art computational techniques. Success in low-temperature modeling work (Year 2) will provide insights into how to overcome fundamental limitations of batteries in cold conditions and will help expand battery use in such conditions.

Presentations

Gering, K. L., “Exploring Electrolyte Properties and Behavior through a Chemical Physics Modeling Approach,” CAES Materials, Modeling, Simulation, and Visualization Workshop, McCall, Idaho, May 13, 2015.

15-146—Tailoring the Kinetic Function of a Surface through Electronic Effects of Nanoscale Architecture

Rebecca Fushimi, Joseph Holles,[1] Michael Glazoff, and Gregory Yablonsky[2]

Nearly 90% of the industrial processes that provide food, fuel, and consumer products rely on catalysis. Many of today's leading chemical transformation technologies remain highly energy intensive, complex, and expensive. In addition, poor selectivity results in waste production and high CO_2 emissions. The U.S. shale gas industry has entered a period of sustained low natural gas prices and growing supply. We may now envision a paradigm shift away from the historical chemical process starting from heavy petrochemical feed-stocks. This project is motivated by the need to shift the focus of industrial processes to build chemical intermediates from more abundant shale gas resources.

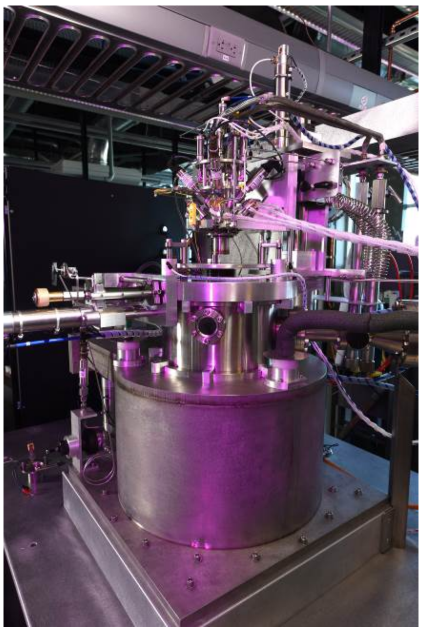

Figure 1. TAP Reactor System acquired during FY 2015. This system is one of three in the United States and unique in the DOE complex.

The surface of a solid catalyst orchestrates the making and breaking of chemical bonds in a complex reaction mechanism. While the variety of catalytic architectures one can create is endless, there are only a few chemical bonds one needs to break/form in the interest of energy transformations: C-H, C-C, C-O, O-H, etc. Specifically, this work is focused on the selective dehydrogenation of light alkanes. This reaction is the first step in upgrading abundant domestic gas resources to higher-value alkenes, which serve as the building blocks of vitally important petrochemicals such as polypropylene and polyacrylonitrile.

While platinum is an excellent metal for C-H bond activation, it binds too strongly to unsaturated intermediates, leading to the formation of coke and deactivation. A general strategy is to alloy platinum with another metal to reduce the bonding strength of unsaturated hydrocarbons. New synthetic advances allow precise engineering of multicomponent metal architectures, and when combining two different metals at the nanoscale, a material with *emergent* electronic properties is created (i.e., new properties that are distinct from the summation of individual parts). For example, the surface electronic states will vary widely when two metals are arranged in an alloy configuration, in a core-shell configuration, or as an assembly of discrete nanoparticles. This work utilizes a unique, low-pressure transient kinetic technique to understand how nanoscale bimetallic architectures, namely core-shell configurations of different precious metals (platinum, palladium, rhenium, gold) and base metals (cobalt, nickel, tin), can be used to direct the activation of light alkanes.

Summary

Significant progress has been made to propel the project into FY 2016. A key task was to purchase and install a temporal analysis of products (TAP) reactor system (Figure 1) to enable transient kinetic studies of core-shell catalysts during subsequent years. This TAP system provides INL and DOE with unique capabilities. Only two other units are in operation in the United States, and fewer than 20 are in operation worldwide. In the future, the

[1] University of Wyoming

[2] Saint Louis University

instrument will serve as the centerpiece of an industrial consortium to support catalyst development efforts in collaboration with U.S. chemical manufacturing leadership.

Prior to commissioning of the INL TAP system, a collaboration was developed with researchers Unni Olsbye and Evgeniy Redekop at the University of Oslo, where an advanced TAP reactor system was recently installed. The principal investigator conducted a two-week research visit to collect experimental data, as well as to develop new research and data-analysis methodologies. The team completed a manuscript titled "Distinguishing Industrial Microporous Materials with Transport/Kinetic Properties Accessed at Low-Pressure Conditions: Methanol to Olefins Catalysts Using Ethylene as a Probe Molecule." This manuscript will be submitted to the peer-reviewed journal *ACS Catalysis*. Similar results of transport/kinetic characterization in metal organic frameworks were presented at the XII European Congress on Catalysis in Kazan, Russia.

Benefits to DOE

Energy supply plays a key role in U.S. security. New catalytic technology is needed that can utilize abundant shale gas resources to replace the conventional production of fuels and chemicals that are currently based on petroleum. This work contributes to fundamental understanding of how catalytic materials can be improved to control a desired sequence of chemical reaction.

Publications

Fushimi, R., J. Gleaves, E. Redekop, X. Wang, Y.-F. Chang, S. Shekhtman, and G. Yablonsky, "Distinguishing Industrial Microporous Materials with Transport/Kinetic Properties Accessed at Low-Pressure Conditions: Methanol to Olefins Catalysts Using Ethylene as a Probe Molecule" *ACS Catalysis,* in preparation.

Fushimi, R., J. Gleaves, and G. Yablonsky, "Experimental Methods for the Determination of Parameters," *Multiphase Catalytic Reactors: Theory, Design, Manufacturing and Applications*, Z. Onsan and A. Avci, eds., Hoboken, New Jersey: Wiley, 2016, accepted for publication.

Presentations

Fushimi, R., E. Redekop, C. Nyapete, J. Gleaves, and G. Yablonsky, "A kinetic fingerprint for distinguishing porous diffusion," XII European Congress on Catalysis, Kazan, Russia, August 30 – September 4, 2015.

Fushimi, R., "Transient kinetic experiments and a new approach to the complexity of industrial catalytic surfaces," Center for Environmentally Beneficial Catalysis, Industrial Colloquium Series, Lawrence, Kansas, September 10, 2015.

15-147—Rare Earth Element Catalysts for Carbon-Based Chemicals

Lucia M. Petkovic, Daniel M. Ginosar, and Maohong Fan[1]

This project studies the production of chemicals and materials from coal and natural gas, strengthens a university collaboration, and builds the DOE talent pipeline in technical areas. This project seeks to develop the background for alternatives to manufacturing opportunities in Wyoming. It targets coal and natural gas, which are resources with significant impact on our nation's economy. In this project, students from the University of Wyoming are mentored by senior INL personnel to perform research work at INL.

Summary

The joint research conducted for this project is aimed at developing technologies that could benefit the current and future missions of DOE by building on critical materials strengths residing at INL. This project is focused on two areas: (a) the production of chemicals and materials from coal and (b) the production of chemicals from natural gas.

Two students from the University of Wyoming were mentored to do research work at INL. One of the students focused on the area of production of chemicals and materials from coal, and the other focused on the production of chemicals from natural gas.

The research completed in the summer of 2015 provided baseline experimental data for the production of chemicals and materials from coal using supercritical toluene. For the research involving natural gas, an existing experimental setup had to be redesigned and adapted for studying reactions involving mixtures of flammables and oxidants such as oxidative coupling of methane (natural gas) to produce ethylene.

Benefits to DOE

This project developed new capabilities to enable the production of fuels and chemicals from coal and natural gas. Production of fuels and chemicals from coal and natural gas, through alternatives to traditional coal and natural gas combustion, reduce the production of greenhouse gases, which is of interest to DOE's environmental mission. In addition, production of fuels and chemicals from domestic resources reduce the U.S. reliance on imported fuels. Furthermore, the DOE Advanced Manufacturing Office is interested in commodity chemicals that can be made in low-energy-intensity processes.

Invention Disclosures

Ginosar, Daniel M., Lucia M. Petkovic, Anne M. Gaffney, and Richard D. Boardman, Catalytic Supercritical Fluid Upgrading of Coal, Invention Disclosure Record BA-865.

[1] University of Wyoming

SECURING AND MODERNIZING CRITICAL INFRASTRUCTURE

13-093—Spectrum Allocation and Communications in Dynamic Spectrum Access Channels

13-118—Geomagnetic Disturbance Field Coupling Measurements on INL Power Grid

14-032—CAN Bus Security across Multi-Sector Platforms

14-035—Safer Energetic Materials – Ignition Prevention with Improper Heating Rate

14-087—Transparent Fiber Reinforcements for Transparent Protection Systems

14-093—All Hazards Critical Infrastructure Knowledge Framework

14-094—SMC Advanced Armor Materials and Systems R&D

15-036—Resilience Metrics Design Establishing the Resilience Benefit of Smart Grid Advancements

15-083—Visualizing Highly Dense Geospatial Data

15-086—Grid Data Analytics Framework

15-096—End-to-End Dynamic Program Analysis for Industrial Control Systems with Concolic Execution

15-097—Security Risks Posed by Convergent Evolution in Industrial Control Systems Internals

15-098—Developing and Demonstrating Cost-Effective Ballistic Protection for Critical Electrical Assets

15-100—RTPS Real-Time Process Simulator

15-106—Automated Security Vulnerability Analyzer for Long-Term Evolution (LTE) Systems - LTE Hack Box

15-107—Advanced Visualization for Simulation and Modeling

15-111—Adversary Signature Development and Threat Analysis

13-093—Spectrum Allocation and Communications in Dynamic Spectrum Access Channels

Hussein Moradi, Brandon Lo, David Couch, Daryl Wasden,[1] and Behrouz Farhang-Boroujeny[2]

The exponential growth of wireless devices and mobile data usage in our nation demands additional spectrum or flexible-use spectrum for high-speed wireless broadband access. Mobile data traffic is predicted to increase by six fold in North America between 2014 and 2020.[3] To meet such a strong demand, the congressional directive in the Spectrum Act of 2012 allows more spectrum bands to be available for flexible uses, which enables spectrum sharing among federal and commercial users. Moreover, the President's Memorandum of 2013[4] states that spectrum sharing should be used to enhance the efficiency among all users subject to interference protection for federal users, especially national-security, law-enforcement, and public-safety users. Nevertheless, the spectrum sharing arrangements with federal incumbents pose a new challenge of achieving the efficiency of spectrum use while protecting the operations of federal users from harmful interference.

The objective of this LDRD is to address this spectrum-sharing problem by novel dynamic spectrum access (DSA) solutions to ensure seamless and secure communications for federal users. DSA has long been recognized as a promising solution for interference mitigation and the enhancement of spectrum utilization.[5] This LDRD effort is focused on five novel DSA approaches: (a) underlay, (b) overlay, (c) secret key, (d) new frequency band, and (e) medium access control (MAC) to achieve spectrum sharing in spectrum for licensed or authorized shared access.

Summary

In the underlay-based DSA, a specific packet format and a packet-detection algorithm are proposed for detecting physical layer packets transmitted under the noise floor on the underlay control channel. Packet detection is performed after the demodulation and the matched filtering of the sampled received signal. For evaluating the performance of the proposed packet-detection method, the theoretical analysis is performed to derive the analytical expressions for the probability of false alarm and the probability of missed detection. Simulation results show that the project's underlay approach achieves DSA by enabling reliable and secure transmissions under the noise floor in terms of low false-alarm and missed-detection probabilities.

In the overlay-based DSA, a novel generalized frequency division multiplexing (GFDM) transmitter design is proposed for DSA based on orthogonal frequency division multiplexing (OFDM) principles. GFDM is suitable for DSA applications due to its low out-of-band emission and high spectral efficiency compared to OFDM. However, GFDM waveforms are periodic signals that can be constructed like OFDM signals. By doing this, low-complexity inverse fast Fourier transform implementation similar to OFDM can be achieved by the rearrangement of discrete Fourier transform/inverse discrete Fourier transform operations. The implementation complexity is further reduced by the smaller filter length of the frequency spreading filter design. The novel concept of this LDRD and the resulting derivations shed light on some interesting properties of GFDM. In particular, the derivation seamlessly leads to an implementation of a GFDM transmitter, which has significantly lower

[1] Colmek, Inc.

[2] University of Utah

[3] Ericsson Mobility, *Ericsson Mobility Report on the Pulse of the Networked Society*, June 2015.

[4] The White House, "Memorandum for June 14, 2013: Expanding America's Leadership in Wireless Innovation," June 2013.

[5] Qing Zhao and B. M. Sadler, "A Survey of Dynamic Spectrum Access," *IEEE Signal Processing Magazine*, Vol. 24, No. 3, pp. 79–89, May 2007.

complexity (0.5 $MN \log_2 N + 2MN$) than what has been reported so far (1.5 $MN \log_2 MN + 2MN$),[6] where M is the number of symbols for each subcarrier and N is the number of subcarriers. Furthermore, the derivation developed in this LDRD facilitates the applications of GFDM to transmissions in multiple-input and multiple-output channels. Therefore, the OFDM-principle-based GFDM design in the overlay approach achieves DSA by providing a low-complexity transmitter design and low out-of-band emission for enhancing spectral efficiency and facilitating spectrum sharing of heterogeneous wireless systems.

In the secret key approach, a novel method for generating a secret key is proposed to augment the security of underlay-based DSA systems. The proposed key generation takes advantage of the channel reciprocity exhibited between two communicating parties. By using real-world measurements, it is found that the strongest path in the channel impulse response can be the main source of allowing an adversary to generate a similar key to gain access to legitimate nodes. This problem is resolved by introducing an augmentation called strongest path cancellation that removes the strongest path from the channel impulse response before key generation. Moreover, the generated keys need not be perfectly the same at the legitimate nodes, thus enabling fault-tolerant, secure communications for the project's underlay-based DSA systems.

In the project's new frequency band approach, the capability of the proposed underlay-based DSA systems is extended to operate in the high-frequency (HF) skywave channels, that is, the utilization of a new frequency band for dynamic spectrum access. It is demonstrated that these proposed underlay-based DSA systems are well suited for the HF communications because they show excellent performance in channels with frequency-selective fading and interference. New algorithms for packet detection, timing recovery, and equalization that are suitable for the HF channel are developed. An algorithm is also developed for optimizing the peak-to-average power ratio of the underlay waveform, resulting in a very low peak-to-average power ratio of about 4 dB. The simulation results obtained during this LDRD using a wide-band HF channel model demonstrate the robustness of this system over a wide range of delay and Doppler spreads.

In the MAC approach, the DSA system operations consist of three main steps: filter bank spectrum sensing,[7] spectrum opportunity prediction, and dynamic channel allocation. First, DSA senses the wideband spectrum to determine the current channel states on the order of milliseconds. Hence, compared to existing wideband spectrum sensing techniques,[8] the project's DSA solution senses wideband spectrum more efficient without incurring additional implementation cost and complexity. Next, the spectrum-opportunity-prediction mechanism predicts the channels that are the least likely to be occupied in the near future for dynamic channel allocation to minimize the possibility of interference and maximize the system capacity. Based on the previous observations and the current channel states, the parameters of traffic patterns and channel activity in spectrum are first estimated and used to regularly update the cognitive prediction model in the real time. This process empowers the prediction with cognition and learning capabilities to adapt to any traffic pattern and transmission activity changes in the spectrum. The prediction model is then used to calculate the probabilities of future traffic patterns and channel availability. Finally, the spectrum bands with the highest probability of availability for the longest period of time in the future are the best candidates for channel allocation and effective transmission to minimize the possibility of unexpected interference.

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[6] N. Michailow, I. Gaspar, S. Krone, M. Lentmaier, and G. Fettweis, "Generalized frequency division multiplexing: Analysis of an alternative multi-carrier technique for next generation cellular systems," *Wireless Communication Systems (ISWCS), 2012 International Symposium on Wireless Communications Systems*, pp. 171–175, August 2012.

[7] B. Farhang-Boroujeny, "Filter Bank Spectrum Sensing for Cognitive Radios," *IEEE Transactions on Signal Processing*, Vol. 56, No. 5, pp. 1801–1811, May 2008.

[8] Hongjian Sun, A. Nallanathan, Cheng-Xiang Wang, and Yunfei Chen, "Wideband spectrum sensing for cognitive radio networks: a survey," *IEEE Wireless Communications*, Vol. 20, No. 2, pp. 74–81, April 2013.

Benefits to DOE

This research contributes to DOE's mission by enhancing the security of energy infrastructure and public safety communications by developing solutions to implement the U.S. Office of Science and Technology Policy, "Presidential Memorandum-unleashing Wireless Broadband Revolution." Additionally, this project will benefit federal agencies with operations in the 1755- to 1850-MHz bands, including the Departments of Energy, Defense, Homeland Security, and Justice, as well as the Federal Aviation Administration and the National Aeronautics and Space Administration.

Publications

Deaton, Juan, Lynda Brighton, Rangam Subramanian, Hussein Moradi, and Jose Loera, "Accelerating Spectrum Sharing Technologies," *IEEE Communications Magazine*, Vol. 51, No. 9, September 2013.

Farhang-Boroujeny, Behrouz and Hussein Moradi, "Derivation of GFDM Based on OFDM Principles," *Proceedings of IEEE International Conference on Communications (ICC), 2015*, London, United Kingdom, June 2015, pp. 2680–2685.

Laraway, Stephen Andrew, Hussein Moradi, and Behrouz Farhang-Boroujeny, "HF Band Filter Bank Multi-Carrier Spread Spectrum," *Proceedings of MILCOM 2015,* Tampa, Florida, October 2015, to appear.

Majid, Arslan, Hussein Moradi, and Behrouz Farhang-Boroujeny, "Secure Information Transmission in Filter Bank Multi-Carrier Spread Spectrum Systems," *Proceedings of MILCOM 2015,* Tampa, Florida, October 2015, to appear.

Moradi, Hussein, Brandon F. Lo, David Couch, Lloyd Landon, Tarek Haddadin, Stephen Andrew Laraway, Arslan Majid, Taylor Sibbett, Daryl L. Wasden, and Behrouz Farhang-Boroujeny, "An Underlay Control Channel for Dynamic Spectrum Access: Packet Design, Implementation, Analysis, and Experimental Results," *IEEE International Conference on Computer Communications (INFOCOM) 2016*, submitted for publication.

Wasden, Daryl L., Hussein Moradi, and Behrouz Farhang-Boroujeny, "Comparison of Direct Sequence Spread Spectrum Rake Receiver with a Maximum Ratio Combining Multicarrier Spread Spectrum Receiver," *Proceedings of IEEE International Conference on Communications (ICC), 2014*, Sydney, Australia, June 2014, pp. 4656–4661.

Presentations

Farhang-Boroujeny, Behrouz and Hussein Moradi, "Derivation of GFDM Based on OFDM Principles," IEEE ICC 2015, London, United Kingdom, June 8–12, 2015.

Laraway, Stephen Andrew, Hussein Moradi, and Behrouz Farhang-Boroujeny, "HF Band Filter Bank Multi-Carrier Spread Spectrum," MILCOM 2015, Tampa, Florida, October 26–28, 2015.

Majid, Arslan, Hussein Moradi, and Behrouz Farhang-Boroujeny, "Secure Information Transmission in Filter Bank Multi-Carrier Spread Spectrum Systems," MILCOM 2015, Tampa, Florida, October 26–28, 2015.

Moradi, Hussein, "National Security/Emergency Preparedness: Technical Execution Discussion," Joint Program Office (JPO) Presentation, June 26, 2013.

Moradi, Hussein, "DEA Spectrum Communications Research: Video Surveillance," Drug Enforcement Administration Presentation, July 29, 2013.

Wasden, Daryl L., Hussein Moradi, and Behrouz Farhang-Boroujeny, "Comparison of Direct Sequence Spread Spectrum Rake Receiver with a Maximum Ratio Combining Multicarrier Spread Spectrum Receiver," *IEEE ICC 2014*, Sydney, Australia, June 10–14, 2014.

13-118—Geomagnetic Disturbance Field Coupling Measurements on INL Power Grid

Shawn West, Mack Grady,[1] Scott McBride, Tom Baldwin, Carol Reid, David Kelle, and Dave Fromme[2]

For understanding and predicting the coupling effects of geomagnetic-induced current (GIC) into a utility-scale grid, this project's researchers developed and installed a geomagnetic disturbances (GMD)/GIC measurement recording system on the INL power grid. INL has tested the effects of GMDs caused by solar storms on critical power system components using INL's full-scale power grid. This project measures and correlates geomagnetic storms with the resultant phenomena of GIC on INL's 138-kV transmission grid. Because electric utilities are unable to perform these tests on their operating systems, the INL power grid provides a unique opportunity for research and validation. Until INL's LDRD, utility companies have relied on models and theories to help mitigate the possible effects of solar storms. The ability to understand, predict, and mitigate GMD/GIC problems on INL's grid will assist the larger-scale utilities to understand, predict, and mitigate effects in the national grid system. This project developed analysis procedures and methods to detect the onset, and determine the severity, of GIC resulting from geomagnetic storms.

Summary

The INL GIC measurement system measures and correlates GMD effects imposed by solar storms on the INL grid system, allowing INL engineers to understand the phenomena, as it affects INL, to determine what (if any) damaging effects are possible and to develop and test mitigations, as necessary.

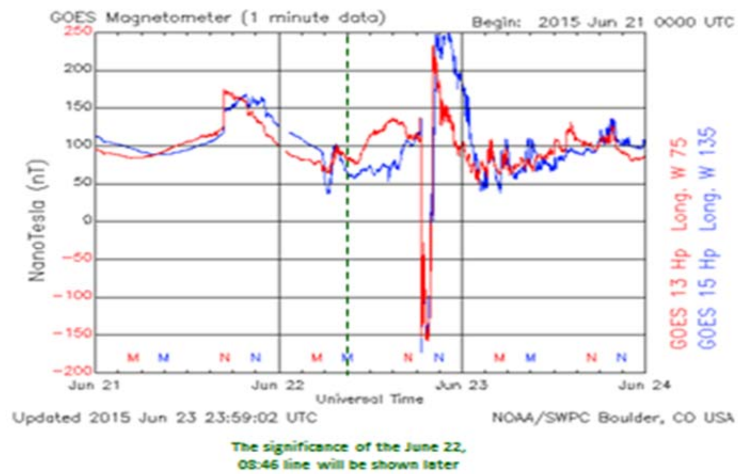

Figure 1. Relative GMD fluxgate measurements of solar storm that occurred on June 22, 2015.

The project is obtaining GIC measurements from three-phase, alternating-current, high-voltage, and medium-voltage INL transformers, transmission lines, and power infrastructure simultaneously with co-located geomagnetic-effect sensors (mass flow sensors). Current-flow sensors have been placed on available transformer-phase and ground circuits on the INL transmission line in time to observe the peak of the solar storm cycle predicted to occur from December 2013 through December 2015. Through the array measurements of electric and magnetic fields, detailed waveforms of the phase voltages, line, and neutral currents have been obtained and analyzed. Characteristics of the waveforms have been used to develop methods for detection and analysis of GIC impacts on the INL power grid. These methods can be applied to the electric utility industry to detect and protect against grid transformer damage caused by GIC resulting from GMD. Examples of the correlation of solar storm activity and the resulting measured GIC impact on the INL grid are shown in Figures 1 and 2, respectively.

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[1] Baylor University

[2] Scientific Applications & Research Associates

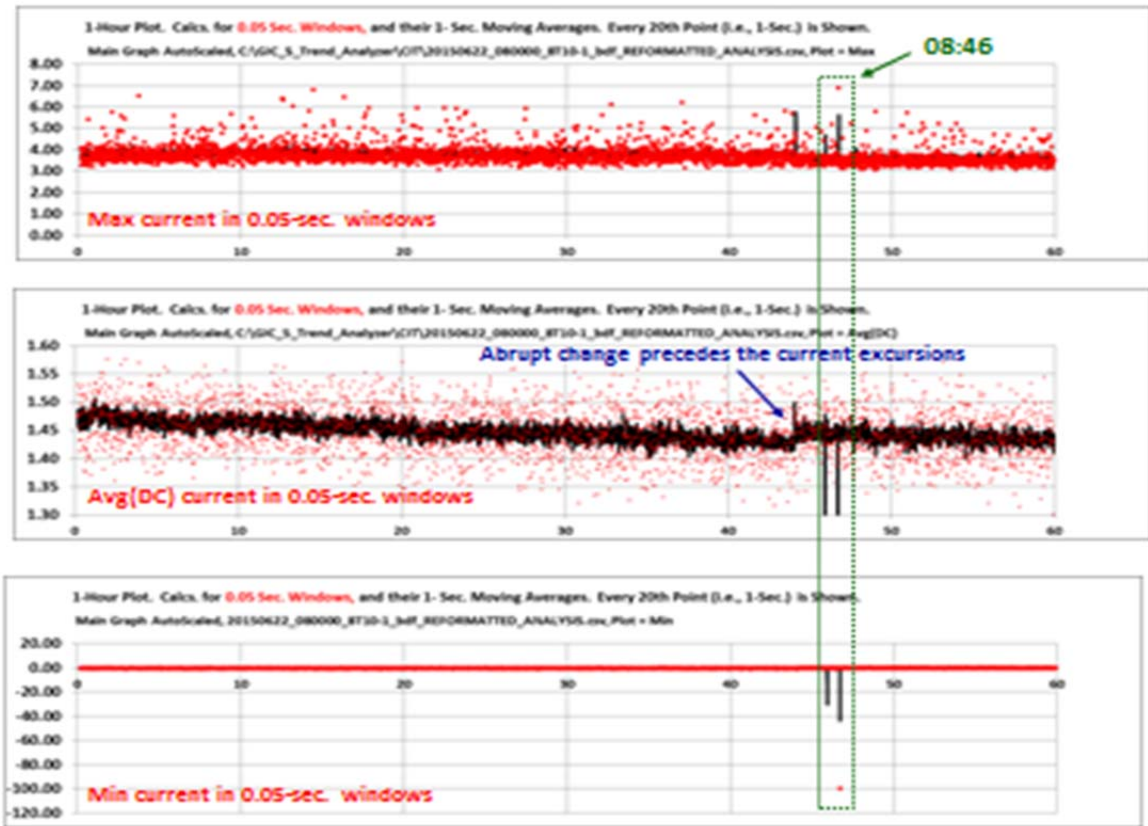


Figure 2. Ground-induced current on INL power grid correlated to solar storm that occurred on June 22, 2015.

Benefits to DOE

The resulting technologies of this project will benefit national security by enhancing the reliability and resilience of energy supplies for our nation's domestic and foreign military installations. This LDRD is developing analysis products that will be deployable to power utilities to assess solar storm impacts to utility systems for critical infrastructure protection. The resulting technology will significantly advance the ability to monitor the electric power grid with benefits to both microgrid and smart grid research and implementation activities that rely on sensor-based feedback to increase system reliability, efficiency, and resilience.

Publications

West, S., S. McBride, and A. Walker, "INL GMD Measurement System," report to industry, in press.

Presentations

West, S. and A. Walker, GMD GIC INL DTRA SANDAQ, GMD Conference, Idaho Falls, Idaho, August 2013

West, S., D. Kelle, M. Grady, and S. McBride, "INL Full-Scale Geo-Magnetic Disturbance Ground Induced Current LDRD," INL GMD Workshop, Idaho Falls, Idaho, April 2015.

14-032—CAN Bus Security across Multi-Sector Platforms

Jonathan Chugg and Kenneth Rohde

The controller area network (CAN bus) protocol—developed during the early 1980s, first released in 1987, and used in a small number of passenger cars—controls the CAN bus in a modern automobile, which may contain 50 or more electronic control units. These electronic control units support a number of different subsystems, including control modules for the engine, powertrain, transmission, antilock brakes, airbags, power steering, cruise control, door locks, windows, audio system, battery, and charging system. The CAN bus protocol also supports many different protocols that are used in a wide variety of areas, including automobiles, road transportation, rail transport, industrial automation, power generation, maritime activities, military vehicles, aviation, and medical devices. This research is being performed to discover new technologies capable of enhancing the cybersecurity of the CAN bus within a typical passenger vehicle, with applications that can also address aerospace-, rail-, and maritime-related transportation systems.

Summary

The first year's research focused on accomplishing two goals. The first was to discover whether the wireless communications link used in the tire-pressure-monitoring system of a modern vehicle is vulnerable to cyber exploitation through its core CAN bus network. INL research is emphasizing the discovery and subsequent solutions to complex attack vectors that have yet to be publicly disclosed. The second goal was to identify the possibility of circumventing CAN bus gateways (modules that shift information between different CAN bus networks) to migrate from one CAN bus network to another. Using an attack initiated on a sub-CAN bus network, research is intended to examine whether an attacker can gain access through CAN bus gateways to more critical systems. The first year of this LDRD developed laboratory capabilities that included a vehicle test prototype, which required:

- Development of software to decode tire-pressure-monitoring system signals using a software-defined radio
- Completion of initial proof-of-concept CAN bus message spoofing
- Procurement of a modern test vehicle CAN bus system
- Development of a prototype hardware/software device to monitor and "fingerprint" CAN bus networks
- Procurement of test vehicle reprogramming and diagnostics tools.

This vehicle test prototype consists of the electronics of a salvaged vehicle fastened to a display board along with a CAN bus prototype device that the research team is continuing to develop. This module will be used as a basis for the development of a CAN bus experimental environment to monitor up to three networks and provide alerts on abnormalities. Initial experiments to migrate from one CAN bus network to another have determined that CAN bus gateways only allow a limited set of messages to transition across other CAN bus networks.

During the second year of this LDRD, the research team continued to conduct proof-of-concept experimentation to explore new emerging technologies employed in CAN bus devices across the many transportation sectors. Research included experimentation with new remote wireless and wired capabilities that will soon be employed in the transportation sector, including interconnects between vehicles, charging stations, and the electric grid (Figure 1). Successes include identification of modules responsible during charge and demodulation of CAN bus signals across the charge-and-demodulation interface. Future research will focus on reverse engineering firmware and modules, identifying vulnerabilities in each of the three systems during charging, and developing scenarios and simulations for cyber-attacks.

Figure 1. Overview of vehicle-to-vehicle and vehicle-to-infrastructure interconnects.

Benefits to DOE

The research being performed will enhance the cybersecurity of all sectors of the nation's critical infrastructure that utilize CAN bus networks, including the transportation, law-enforcement, energy, and nuclear-security sectors. This research, initially focused on a typical passenger vehicle, is intended to result in deployed cybersecurity innovations that are used in all CAN bus networks. A final goal in the research is to identify and mitigate security flaws in an electric vehicle, charging station, and the electric grid and the interconnects among all three systems.

Presentations

Chugg, J., Battelle Energy Alliance Science and Technology Committee, INL, Idaho Falls, Idaho, July 24, 2014.

Chugg, J., "Vulnerability Analysis of CAN Bus Networks," U.S. Secretary of Energy (Ernest Moniz), INL, Idaho Falls, Idaho, August 19, 2014.

Chugg, J., "Vulnerability Analysis of CAN Bus Networks," National Association of Regulatory Commissioners, INL, Idaho Falls, Idaho, August 21, 2014.

Chugg, J., "Vulnerability Analysis of CAN Bus Networks," DOE-NE, Germantown, Maryland, August 25, 2014.

Chugg, J., "Vulnerability Analysis of CAN Bus Networks," Wisconsin Energy Institute, INL, Idaho Falls, Idaho, September 8, 2014.

Chugg, J. and K. Rohde, “Vehicle (In)Security,” IAEA International Conference on Computer Security in a Nuclear World, Vienna, Austria, June 2015.

Chugg, J., and K. Rohde, “Strategic Advisory Committee Poster Session,” Energy Innovation Laboratory at INL, Idaho Falls, Idaho, June 12, 2014.

Rohde, K., “Current Cyber Security Efforts,” United States Council for Automotive Research: Grid Interaction Tech Team, Energy Systems Laboratory Building at INL, Idaho Falls, Idaho, August 2014.

Invention Disclosures and Patents

Rohde, K. and J. Chugg, Invention Disclosure Record BA-814.

Rohde, K., J. Chugg, R. Condit, and J. Verba, Invention Disclosure Record BA-858.

Rohde, K. and J. Chugg, CAN Bus Network Safety and Security System, Provisional Patent 2939-P12608US.

14-035—Safer Energetic Materials – Ignition Prevention with Improper Heating Rate

Michael Daniels, Michelle Pantoya,[1] and Ron Heaps

The objective of this project is to include an additive (or modify the oxidizer) in composite energetic materials that allows energetic materials to ignite only when they are heated at a specific (high) heating rate. These enhancements to energetic materials will reduce the hazards related to environmental conditions that could cause the energetic materials to ignite from electrostatic discharge (ESD) or when the fuel reaches its melting point during storage or transport. These innovative additives are intended to enable the energetic mixtures to respond only to specific on-command ignition stimuli while preventing initiation of the energetic materials when exposed to any other stray or unintentional stimuli. Advancements in materials chemistry enable this concept to become more feasible and also create opportunities for innovations in the tune-ability of the effectiveness of composite energetic materials.

Summary

The approach of this project was to start with a patent-pending mixture developed for its increased safety to ESD stimuli. The mixture is composed of micron-scale aluminum particles combined with copper-oxide particles and ESD-inhibiting materials. This mixture was shown to be desensitized to ESD ignition and to have a negligible effect on the mixture's overall combustion behavior. To further develop a safer material, experiments were conducted with a series of additives to seek energetic material mixtures that would be inert when subjected to slow heating processes (i.e., simulating an accidental fire). Through experimentation with various compositions of materials (Figures 1 and 2), significant progress was made in developing a new methodology to tailor a thermite reaction for safer use during multiple applications. Specifically, this research identified an electrical conductivity regime that promoted ESD insensitivity (i.e., ~ 0.01 S/cm) and explored several additives to desensitize compositions to prevent high-energy evolution during slow heating conditions, thus simulating an accidental fire. The mechanism for neutralizing the formulation was identified through deactivating thermal decomposition and rendering the mixture too fuel rich to achieve sustained propagation. These material discoveries will be further examined under other heating-rate (i.e., bake) conditions to better simulate accidental fires representative of a typical hydrocarbon flame, as demonstrated by Babrauska and Peacock.[2]

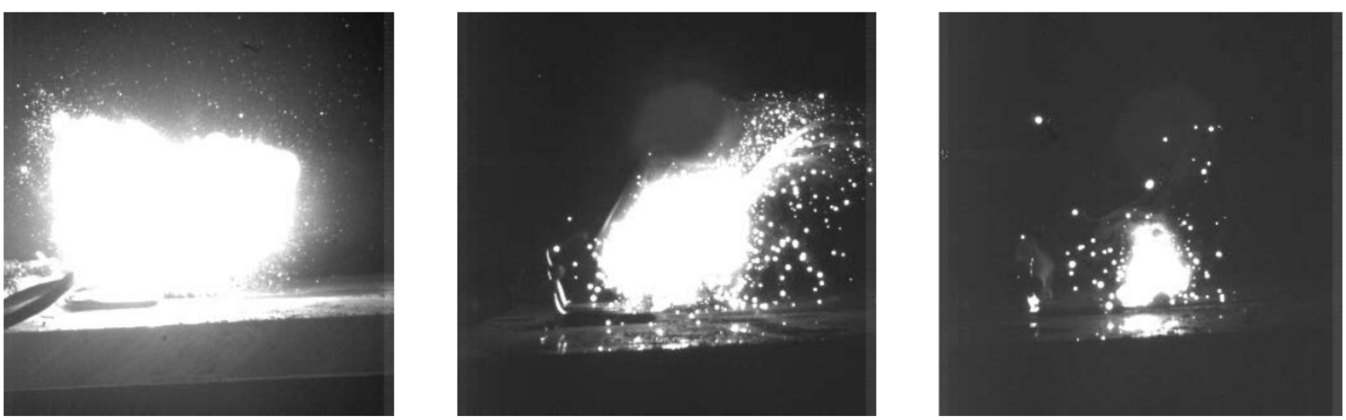


Figure 1. Representative still-frame images of reactions of multiple mixtures of aluminum, copper-oxide particles, and experimental additives.

[1] Texas Tech University

[2] V. Babrauska and R. D. Peacock, "Heat Release Rate: The Single Most Important Variable in Fire Hazard," *Fire Safety Journal,* Vol. 18, pp. 255–272, 1992.

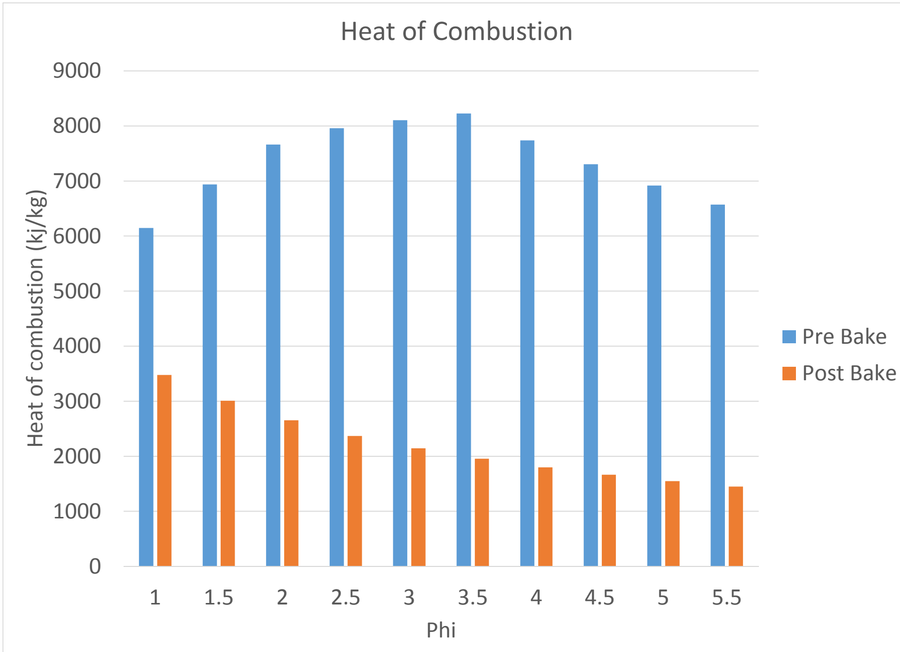


Figure 2. REAL code simulations for the reaction shown above with varying material compositions.

Benefits to DOE

This project has the potential to greatly improve the safety of personnel in DOE, the U.S. Department of Defense, and the Department of Homeland Security who routinely use energetic materials for physical security, emergency response, and material disposition. These novel materials also present the potential for improving the safe use, shipping, and storage of energetic materials in applications associated with infrastructure construction, mining, and emergency first responders.

Publications

Bellow, M., K. Poper, M. Daniels, and M. Pantoya, "Controlling Accidental Fire Ignition Safety of a Thermite with Ammonium Nitrate Additive," *ACS Sustainable Chemistry and Engineering,* to be submitted.

Collins, E., B. Skelton, M. Pantoya, F. Irin, M. Green, and M. Daniels, "Ignition Sensitivity and Electrical Conductivity of a Composite Energetic Material with Conductive Nanofillers," *Combustion and Flame*, in review.

Poper, K., E. Collins, M. Pantoya, and M. Daniels, "Controlling the Electrostatic Discharge Ignition Sensitivity of Composite Energetic Materials Using Carbon Nanotube Additives," *Journal of Electrostatics,* Vol. 72, pp. 428–432, 2014.

Steelman, R., M. Daniels, and M. Pantoya, "The Influence of Particle Size on the Electrostatic Discharge Desensitization to Ignition," Journal of Applied Physics, to be submitted.

14-087—Transparent Fiber Reinforcements for Transparent Protection Systems

Thomas Lillo, Michael Bakas, and Henry Chu

Continuous-fiber-reinforced composites are considerably stronger than nonreinforced materials, resulting in increased performance with less weight. Applications requiring transparent materials have not benefited from continuous-fiber reinforcement due to optical transparency requirements. This project endeavors to address this deficiency by developing new transparent fibers of ceramic materials (i.e., aluminum oxynitride [AlON]) with increased strength, general corrosion resistance, and high-temperature degradation resistance. These novel materials will allow the development of transparent protection systems with greatly improved performance for government and civilian facilities and vehicles. This project's objective is to evaluate high-temperature, chemical processes to convert nontransparent continuous fibers to transparent continuous fibers for use as reinforcement in transparent protection systems.

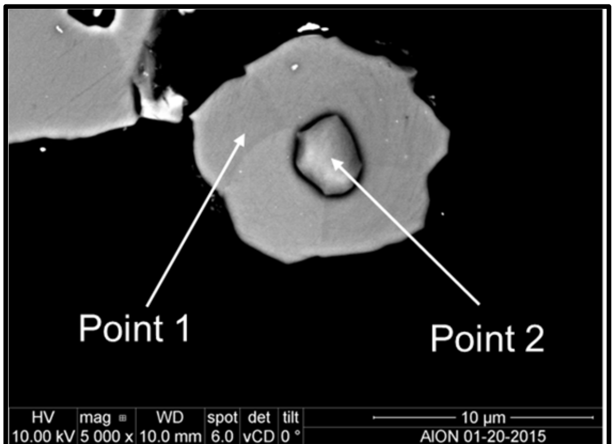
Summary

The experimental approach for this project involved the evaluation of processes to convert a precursor, commercially available, nontransparent fiber to the desired transparent fiber through high-temperature processes. Conversion processes were based on the carbothermal reduction of Al_2O_3 to produce AlON fiber. Modeling results and a literature review identified compositions of prospective furnace atmospheres that were evaluated experimentally.

A two-step conversion process was developed, with each step requiring a different furnace atmosphere to control the phases present during each step of the conversion process. Processing schedules were developed that formed a considerable amount of AlON with residual Al_2O_3 remaining at the core of the converted filament. Figure 1(a) is a high-magnification image taken by a scanning electron microscope (SEM), clearly showing the AlON outer conversion product on a residual core of Al_2O_3, as determined by the x-ray energy dispersive spectroscopy compositional analyses at Points 1 and 2. Modifications to the processing schedule (e.g., conversion time and temperature) are expected to result in complete conversion to AlON.

Additionally, sintering together of the filaments within the fiber (the starting Al_2O_3 fiber is composed of 400 Al_2O_3 filaments that are approximately 10–12 µm in diameter) due to the high processing temperature was observed, Figure 1(b), and severely degraded the flexibility of the converted fiber. Adjustments were made to the processing schedule and furnace processing atmosphere, which inhibited sintering of the filaments during processing, restoring the flexibility of the converted fiber to a large extent.

Overall, this LDRD project proved that the processing methodology developed is capable of converting continuous Al_2O_3 fiber into continuous AlON fiber that retains most of the flexibility necessary for handling and subsequent incorporation into next-generation armor and blast-protection systems. However, significant development and optimization remain before optical properties of the converted fiber can be evaluated. Demonstration of optical transparency of the converted fiber will then allow development of advanced transparent systems with improved performance. Additionally, the results of this work have implications in the production of AlON powder for transparent, monolithic AlON panels and the production of short AlON fibers (up to ~25 mm in length) for transparent reinforcement of transparent polymeric materials and glasses.



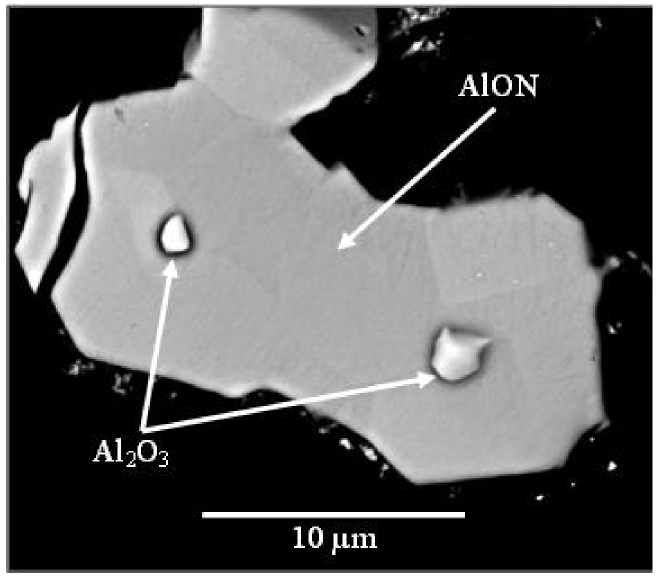
Point 1 (AlON)

Element	Wt %	At %
N K	01.88	02.93
O K	32.11	43.77
AlK	65.67	53.07

Point 2 (Al_2O_3)

Element	Wt %	At %
N K	00.36	00.55
O K	37.15	49.81
AlK	62.08	49.35

(a)



(b)

Figure 1. SEM image of an alumina filament partially converted to AlON with chemical analysis points showing a small residual core of alumina remaining in the converted filament (a) and an SEM image of two filaments that sintered together during conversion to AlON; small residual cores of alumina remain at the center of each filament (b).

Benefits to DOE

To date, this project has made considerable progress toward developing a process to fabricate a new class of optically transparent fibers that can be used in a variety of transparent protection applications relevant to the security of nuclear facilities, as well as various other civilian and law-enforcement structures. Furthermore, many military and civilian protection applications will benefit from a new class of ballistic protective transparent fibers.

Invention Disclosures

Invention Disclosure Record, Tracking No. 3490.

14-093—All Hazards Critical Infrastructure Knowledge Framework

Ryan Hruska, Cherrie Black, and Milos Manic[1]

The objective of this research project was to develop advanced-knowledge-discovery and decision-support methodologies to improve the capability of the United States to conduct infrastructure interdependency analysis to better prepare for, protect against, respond to, recover from, and mitigate all hazards. This project has two main objectives: (a) development of a knowledge model framework for critical infrastructure and (b) development of adaptive hybrid data and expert-driven algorithms for online learning of infrastructure characteristics.

Summary

Technical progress made toward meeting the objectives of this project has included the following in the area of the knowledge model framework:

- Enhanced and completed dependency profile generation for a range of lifeline infrastructures
- Developed prototype geospatially enabled knowledge framework utilizing graph-style database architecture, including:
  - Ingested structured infrastructure information from numerous open-source and government-owned databases
  - Generated proof-of-concept dependency models
- Developed a prototype dependency reasoning model for energy-sector infrastructure.

Technical progress made toward project objectives in the area of text analytics included the following:

- Refined natural language processing techniques for extracting infrastructure information from unstructured text; these techniques consisted of:
  - Named entity recognition for critical infrastructure facilities (water and energy sectors)
  - Geolocation tagging for spatial information extraction
- Refined the prototype automated document-processing architecture for unstructured text
- Automated population of the knowledge framework architecture from unstructured text.

Technical progress made toward project objectives in the area of visualization included development of a prototype graph and geospatial-visualization application.

Benefits to DOE

A major element of the DOE, U.S. Department of Homeland Security, and INL missions is to ensure productive, optimal, and secure use of U.S. energy and critical infrastructure resources. This LDRD project has benefited INL by developing advanced-knowledge-discovery and decision-support methodologies to understand the complex interdependent relationships within these integrated systems, as well as their vulnerabilities to threats and hazards. By developing these methodologies and demonstrating the ability to solve these complex analytical challenges, the status of DOE and INL as a research leader in critical infrastructure protection will be enhanced.

[1] Virginia Commonwealth University

Publications

Amarasinghe, K., R. Hruska, and M. Manic, “Selection of Optimal Dimensionality for Text Document Content Classification Using Genetic Algorithms,” submitted to IEEE SSCI 2014.

Hruska, R., C. Tuchez, and M. Manic, “Extracting Infrastructure from Web Content Using Natural Language Processing,” submitted to IEEE SSCI 2014.

Presentations

Amarasinghe, K., M. Manic, and R. Hruska, “Optimal Stop Word Selection for Text Mining in Critical Infrastructure Domain,” IEEE Resilience Week, Philadelphia, Pennsylvania, August 2015.

Hruska, R., “Knowledge Framework for Critical Infrastructure Analysis,” DHS Dependency Workshop Series, Idaho Falls, Idaho; Chicago, Illinois; and Washington, D.C., 2015.

Hruska, R. and M. Klett, “Knowledge Framework for Critical Infrastructure Analysis,” IEEE Resilience Week, Denver, Colorado, August 2014.

Hruska, R. and S. Staples, “Natural Language Processing for Critical Infrastructure All Hazards Analysis,” IEEE Resilience Week, Philadelphia, Pennsylvania, August 2015.

Klett, M., “ICSJWG Emerging Research: Infrastructure Threat Recognition, Resilience and Restoration,” ICSJWG Emerging Research Panel Discussion, Washington, D.C., June 2015.

14-094—SMC Advanced Armor Materials and Systems R&D

Michael Bakas, Thomas Lillo, and Henry Chu

High-hardness ceramics, such as alumina (Al_2O_3), silicon carbide (SiC), or boron carbide (B_4C), are often used in advanced-armor systems. Because of inherent brittleness, these ceramics have to be bonded to or encapsulated in metals or laminated composites in order to form effective armor systems. Chemical adhesives are generally used to bond highly dissimilar materials such as ceramic to metal. However, bond strength of most chemical adhesives is generally weak. This research project focuses on developing a metallic bonding methodology to form a stronger joint between the inert SiC and standard armor steel, resulting in a higher performance armor system.

Summary

The metallic bonding methodology consisted of two material- and process-development steps. The first step was to develop a thin metallic coating and associated deposition method that would form a strongly adhered metallized layer on the surface of the SiC. The second step was to develop a braze-filler compound that would bond to the pre-deposited metallic coating and then to the steel substrate.

The metallic coating developed was an iron-silicon-molybdenum compound with an organic carrier that was brushed on the SiC surface and then heated in an oxygen-free atmosphere to form the metallized coating (see Figure 1).

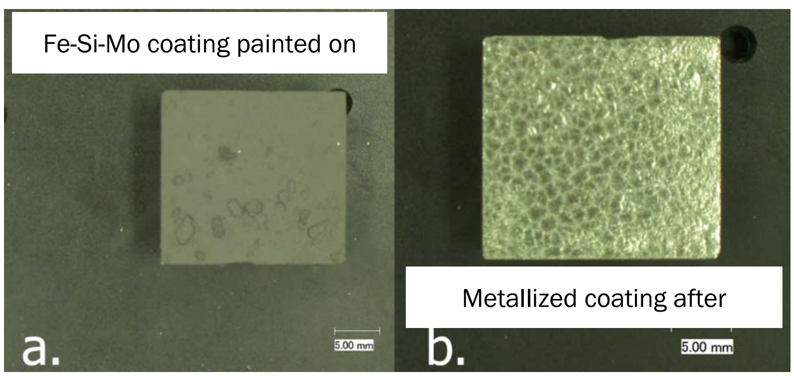


Figure 1. Metallized coating.

The braze-filler compound used was AWS BAg-7, a commercial-grade braze alloy. A standard flux was used to prepare the steel surface by removing organic contaminants and metal oxides. The braze-joining process was performed with a hand-held torch.

Experimental results indicated that, while the braze filler would bond properly to the steel and to the metallized surface of SiC, the large differences in the coefficient of thermal expansion [steel @ 12×10^6 m/(m.k) vs SiC @ 2.8×10^6 m/(m.k)] would subsequently cause the SiC to fracture during cooling. This problem was partially mitigated using a Kovar foil [5×10^6 m/(m.k)] as an intermediate stress-relief layer; but it appeared that the bond integrity was also compromised owing to poor adhesion between the Kovar foil and the metallized coating.

In light of the last result, it is hypothesized that a filler compound based on silver-copper-tin-manganese alloy designed for difficult-to-wet metals may be a potentially better braze-filler material to be used with the iron-silicon-molybdenum metallized coating and Kovar foil as an intermediate stress-relief layer.

Benefits to DOE

The technologies being developed under this project are aimed at supporting the DOE security mission with the potential to also assist the mission of the U.S. Department of Defense because these technologies can be potentially used in new armor solutions and designs.

This project represents fundamental research in advancing an industrial process to join two vastly dissimilar materials.

Presentations

Bakas, Michael and Henry Chu, "Results of the SMC Advanced Armor and Materials Project," 47th Combined Light Armor Survivability Panel (CLASP) Technical Meeting (sponsored by the Naval Research Laboratory), Phoenix, Arizona, March 23, 2015.

15-036—Resilience Metrics Design Establishing the Resilience Benefit of Smart Grid Advancements

Craig Rieger, Brian Johnson,[1] Kamshad Eshghi,[2] and Tim McJunkin

Smart grids add many more capabilities to measure, control, and manage the generation, distribution, and consumption of electrical power in a manner that is intended to produce a more available, cleaner, stable, and economical supply of electricity. The power of additional information is obvious (e.g., optimization of transmission assets, integration of greater renewable generation, and economic assessments put into the hands of consumers). However, the counterpoint is a more complex and computerized system with more potential cyber and physical vulnerabilities and the additional human performance demands on the people monitoring and making operational decisions amid a plethora of new data.

Resilience seeks to optimize when possible but to never sacrifice operational minimums that risk large economic and societal costs through unintentional introduction of brittleness. To measure a system with respect to resilience, a set of measurable and comparable metrics needs to be established in detail. This effort sets out research to evolve a set of qualitative resilience measures into resilience performance metrics for the smart electric grid through the identification and mapping of the principles of resilience to quantitative measurements of resilient control systems.

Summary

Prior work in the area of resilient control systems has provided a number of technology-specific metrics to weight performance and benefit. However, a holistic strategy for benchmarking performance and resilience contributions is nonexistent. In particular, such a holistic strategy involves the measurement of business value and system integrity irrespective of the source of the disturbance, whether from the security, damaging-story, or human-interaction realms. However, with control systems, there is always a physical application that provides the context for what is important or, more specifically, an operational baseline that can be measured. Within the context of this work, the power grid is used as the domain of choice, but the metrics design philosophy can be applied in other domains.

Referring to Figure 1, the initiators of disturbance are placed in terms of cognitive, cyber-physical sources. In all cases, the effects of these disturbances can be normalized based on time and data integrity. Time, both in terms of delay of mission and communications latency, and data, in terms of corruption or modification, are normalizing factors. In general, the idea is to base the metric on "what is expected" and not necessarily the actual initiator that caused the degradation. To implement metrics, this project is developing the characteristics of resilience agents, which offer a notional framework for distributed monitoring and analysis of precursors to disrupting events. Within these agents, the project is evaluating not only physical systems, but also cyber systems and the hybrid interplay between the two (but not the cognitive element at this point). For this work, there are four separate attributes of such an agent: smart signal stability, transient stability, communications latency, and degradation assessment.

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[1] University of Idaho

[2] Bonneville Power Administration

The work to date has involved the Matlab/Simulink® simulation of a standard Institute of Electrical and Electronic Engineers "14" bus system to evaluate its beneficial attributes. With validity established and metrics refined for this system, a scaled-up implementation will be developed within a real-time digital simulator. The methodologies and simulation designed for Simulink are directly extensible for export into the real-time digital simulator for this effort. The resulting testing will demonstrate the large-scale benefit of the metrics and will provide a compelling case for extension to real-world assets.

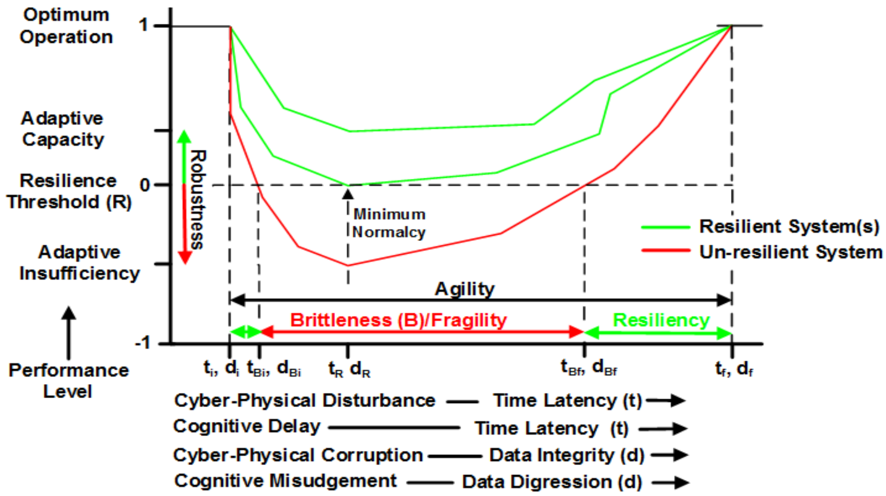

Figure 1. Disturbance and impact resilience evaluation curve.

Benefits to DOE

The integration of cyber-physical protections within the automated systems we depend upon is critical to ensure the viability of these systems in light of the potential for natural catastrophes or malicious action. Presidential Policy Directive 21, "Critical Infrastructure Security and Resilience," recognized the need to advance R&D for resilient critical infrastructure. With the advancement of a smart grid, distributed energy resources, and the resulting added complexity, the ability to evaluate enhancements and measure system performance in real time are necessary to ensure resilience. The resulting resilience metrics basis will be used to establish priorities for implementation and proactively recognize events before precipitating cascading events. This project provides a proof-of-concept to validate a metrics proposition to address these needs.

Publications and Proposals

Eshghi, K., B. K. Johnson, and C. G. Rieger, "Power System Protection and Resilient Metrics," *Resilience Week 2015*, August 2015.

Eshghi, K., B. K. Johnson, and C. G. Rieger, "Resilient Metrics for Power System Operations and Protection," *IEEE Transactions on Smart Grid*, abstract approved and final paper under review.

Rieger, Craig, Department of Energy Grid Modernization Lab Consortium Foundation Proposals in control theory and resilient communications modeling, including INL efforts on resilience metrics.

Rieger, Craig, "Resilience Metrics to Correlate the Cognitive, Cyber-Physical Complexities of Critical Infrastructure" Proposal Submitted to the National Science Foundation, Critical Resilient Interdependent Infrastructure Systems and Processes.

Rieger, Craig, "Resilient, Multi-scale Agent Dynamical System (ReMADS)," Concept Paper Submitted to the Advanced Research Project Agency- Energy, Network Optimized Distributed Energy Systems.

Presentations

National Workshop on Resilience Research for Critical Infrastructure approved and financed by the National Science Foundation.

Research and Development Panel Discussion, Industrial Control System Joint Working Group Conference, Washington, D.C., June 23, 2015.

15-083—Visualizing Highly Dense Geospatial Data

Shane Cherry and Robert Edsall

There is a need to improve the ability to make decisions and analyze risk associated with protective and support measures related to man-made and natural threats to critical infrastructure. Analysts, responders, and decision-makers have many disparate data sources associated with critical infrastructures available to them. The scale of data is staggering, and the ability to collect data is increasing at a faster rate than the ability to analyze them. New methods are required that will allow the analyst to examine massive, multidimensional, multisource, time-varying information streams, such as those shown in Figure 1, to make decisions in a time-critical manner. Because many of these data are georeferenced, it stands to reason that geographical information system tools can be used as the basis for analysis and visualization of these data in order to convert them to actionable information. However, these tools begin to lose value when the available information becomes so dense that it can no longer be easily understood by the human user of the system. To this end, enhanced information visualization capabilities are needed to aid in making quick and effective decisions. In the context of this effort, "visualization" refers to a process of thinking that is aided by such tools—the recognition of patterns, trends, associations, and outliers by interactive digital displays, with the intended result of ideation and hypothesis generation, which then may drive further investigation or confirmation.[1] Visualization of complex statistical, temporal, and geographic information is seen as a vital component in understanding that information by an analyst, regardless of the domain or context.[2] In the context of the homeland security mission, the creation and adoption of innovative visualization tools provide solutions to the challenge of comprehending data associated with critical infrastructure vital to homeland security.

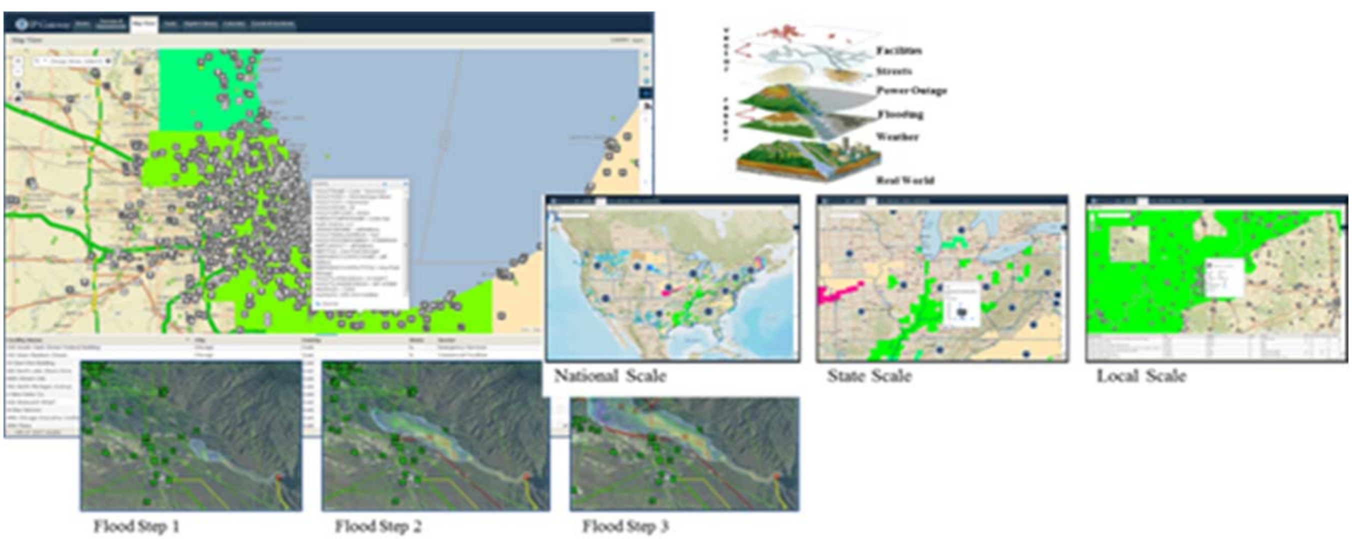

Figure 1. Highly dense, multivariate spatial and temporal data.

[1] Andrienko, G., N. Andrienko, P. Jankowski, D. Keim, M.-J. Kraak, A. MacEachren, and S. Wrobel, "Geovisual analytics for spatial decision support: Setting the research agenda," *International Journal of Geographical Information Science*, Vol. 21, Issue 8, pp. 839-857, 2007.

[2] MacEachren, A. M. and M.-J. Kraak, "Research Challenges in Geovisualization," *Cartography and Geographic Information Science*, Vol. 28, Issue 1, pp. 3–12, 2001.

Summary

Thus far, the project has been directed toward solutions to the visualization—and associated understanding—of data that are dense and irregular in geographic space. Methods to construct an interface that simultaneously provides focus and context of dense, irregular point data representing critical infrastructure facilities have been investigated. An improvement to traditional aggregation techniques, which fail to provide both focus and context, is being developed to make use of geometric binning—a regular tessellation of polygons such as rectangles or hexagons, with each polygon serving as an enumeration unit. This avoids the potential pitfalls of arbitrary enumeration units such as states influencing the patterns that can be visualized. This technique used a mesh of polygons that is overlaid on an irregular and dense point data set, and a summary measure for each polygon (count, sum, average, etc.) is calculated.

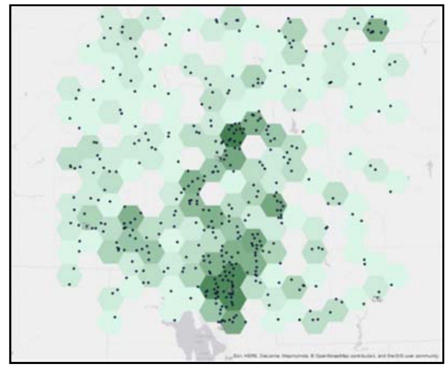

Figure 2. Example of using Delaunay triangulations to reduce clutter in high density

This technique was applied to test irregular data in ArcGIS, drawing a series of layers of hexagons of various scales and aggregating to those units, providing a more data-driven perspective on generalized (context) information, as shown in Figure 2. Next steps will include applying this approach to multidimensional data sets and developing methods to better visualize infrastructure interdependencies.

Benefits to DOE

The results of this effort will directly benefit DOE's mission areas that are associated with the Office of Electricity Delivery and Energy Reliability, are related to enhancing the security and reliability of the energy infrastructure, and facilitate recovery from disruptions to the energy supply. This research also will provide capabilities that could directly support the missions of the Department of Homeland Security, Infrastructure Information Collection Division, and the Office of Cyber and Infrastructure Analysis by providing needed data aggregation, visualization, and analysis capabilities to aid in critical infrastructure protection decision-making processes.

Presentations

Cherry, Shane, "Visualizing Geospatial Data to Support Critical Infrastructure Interdependency Analysis and Situational Awareness," 2nd National Symposium on Resilient Critical Infrastructure, Philadelphia, Pennsylvania, August 18–20, 2015.

15-086—Grid Data Analytics Framework

Rita Foster, Ken Barnes, Shauna Hoiland, Christy Frazee,[1] and Mack Grady[1]

Three objectives of this project are to (1) create a grid analytics framework, including collecting operational and experimental data, to mature grid testing capabilities; (2) use the data to design more precise test setups and validate models, and (3) analyze behavior for the creation of predictive analysis, enabling more resilience applications for the grid, including understanding behaviors and validated models for distributed load/generation to transmission.

Focusing on the ground-induced current (GIC) monitors and the operational data collected during experimentation and normal operations at Scoville, Idaho, samples of data were collected and categorized. These data were used by Mack Grady from Baylor University to identify potential prognostic indicators for geomagnetic disturbances (GMDs) on the electric grid for the purpose of creating mitigating controls for protection of critical infrastructure. Typical power factors were defined in the data dictionary.

The project team created a framework of collected operational and experimental data from the INL Critical Infrastructure Test Range Complex with the appropriate pedigree for sharing, use options, and experiment/operational conditions to enable grid analytics, thus positioning INL for future work on transactive energy. Potential uses of data collected related to power factors were also identified, enabling researchers to know which values are being collected.

Summary

INL created a framework focused on the grid data collected in operations and experimentation of GMDs with the appropriate pedigree for sharing, use options, and experiment/operational conditions to enable grid analytics, positioning INL for future work on transactive energy.

Of the project's three objectives, Objective 1 (create a grid analytics framework) and part of Objective 3 (analyze behavior for the creation of predictive analysis) were completed for GIC/GMD data. The second objective (better test setup and validated models) may continue with analysis of future experimentation configurations to existing data collected.

Benefits to DOE

The data collected has prototype potential detection of GMDs using data from INL's grid and GIC. This detection can trigger mitigations related to digital relays instead of installing neutral ground-blocking devices. Creating prognostic actions from detection aligns with the Grid Modernization Laboratory Consortium activity to improve the ability to identify threats and hazards and create analytic capability.

The creation of repositories for typical grid event data to use as predictive indicators for prognostic protections, model validation, and data correlation will serve the research community and enable sharing of unique grid asset data from other national laboratories and utilities.

Publications

Grady, Mack, "Understanding Power System Harmonics," combined with PCFLO program for loadflow, short circuit, and harmonics analysis, downloadable at http://web.ecs.baylor.edu/faculty/grady/, pending based on harmonic analysis from ongoing efforts.

[1] Baylor University

Grady, Mack, "Update on the INL SANDAQ GIC Monitoring System and Analysis Software, Draft," July 22, 2014.

Presentations

Foster, Rita, Department of Homeland Security Industrial Control System Joint Working Group, June 23, 2015, brief accepted abstract on grid data analytics.

Asian Pacific Resilient Summit and Energy Innovation, August 23, 2015, accepted abstract and poster session included grid data analytics.

Energy Sec – Abstract submitted and accepted on all-hazards agile response included the first use case for grid data analytics – presented September 15, 2105.

15-096—End-to-End Dynamic Program Analysis for Industrial Control Systems with Concolic Execution

Craig Miles, Craig Rieger, and Arun Lakhotia[1]

The United States depends on industrial control systems (ICSs) to safely and securely monitor and control its critical infrastructure. Although today's ICS designs have proven to be reliable, they are vulnerable to some of the same problems encountered with all complex software systems—including software bugs that may have security implications. Due to U.S. dependence on ICSs and the increasing threat to these systems from malware such as Black Energy and Havex, novel and proactive techniques are needed to reduce the vulnerabilities that could be exploited by malicious entities. Concolic execution is a state-of-the-art, program-analysis technique used to detect such bugs and exploitable vulnerabilities in software; therefore, its application to ICS software is desirable.

At its current level of development, concolic execution can only be used to analyze the software running on a single device. In contrast, ICSs are generally composed of multiple devices within a network, with each device running its own software. The software running on the ICS's various devices collectively comprises its software system and would ideally be analyzed as a whole, because bugs and vulnerabilities therein might only be manifested when the devices are working together in concert. Therefore, the purpose of this research is to extend concolic execution such that it can be applied to the software system of an ICS.

Concolic execution serves to discover bugs and vulnerabilities by automatically and repeatedly running a program under many different input values. The goal is to supply a wide enough variety of input values to induce the program into exhibiting many or all of its potential behaviors, including crashes due to bugs and vulnerabilities. The particular input values supplied to the program by concolic execution are generated by analyzing and reasoning about the program's internal logic.

Summary

Progress during this first fiscal year of the project included an evaluation of extensible methodologies that will allow the use of current concolic execution tools to evaluate ICS software on two or more networked devices, such as those shown in Figure 1. The figure shows a control system composed of two controller devices that collectively maintain the fluid level of a tank. However, due to a programmer error, a check to ensure that the maximum flow rate is never exceeded (shown in the translucent portion of Figure 1) was never implemented, and thus a bad input value to the system can cause the tank to overflow. For concolic execution to discover this bug, it must simultaneously be able to observe the execution of the decision point logic on both controller devices and also the flow of information between the devices. A potential technical solution to this problem—using virtualized ICS devices under a unified hypervisor that correlates concolic network traffic among the devices—was found, and the research team is now exploring how it may be implemented.

Other extensions to concolic execution that will make it compatible with the types of computations commonly performed in ICSs, such as operations on floating point (i.e., non-integer) numbers, were also explored. Additionally, a means to incorporate floating point support into concolic execution was identified, and once implemented, analysis will be able to discover bugs and vulnerabilities in many additional types of control system software.

Finally, additional university involvement was pursued regarding the development of an ICS test platform against which the project's concolic methods may be verified and evaluated. Taken together, the work this fiscal year laid the stepping stones that will enable the development of fundamental advances in the project's coming years.

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[1] University of Louisiana at Lafayette

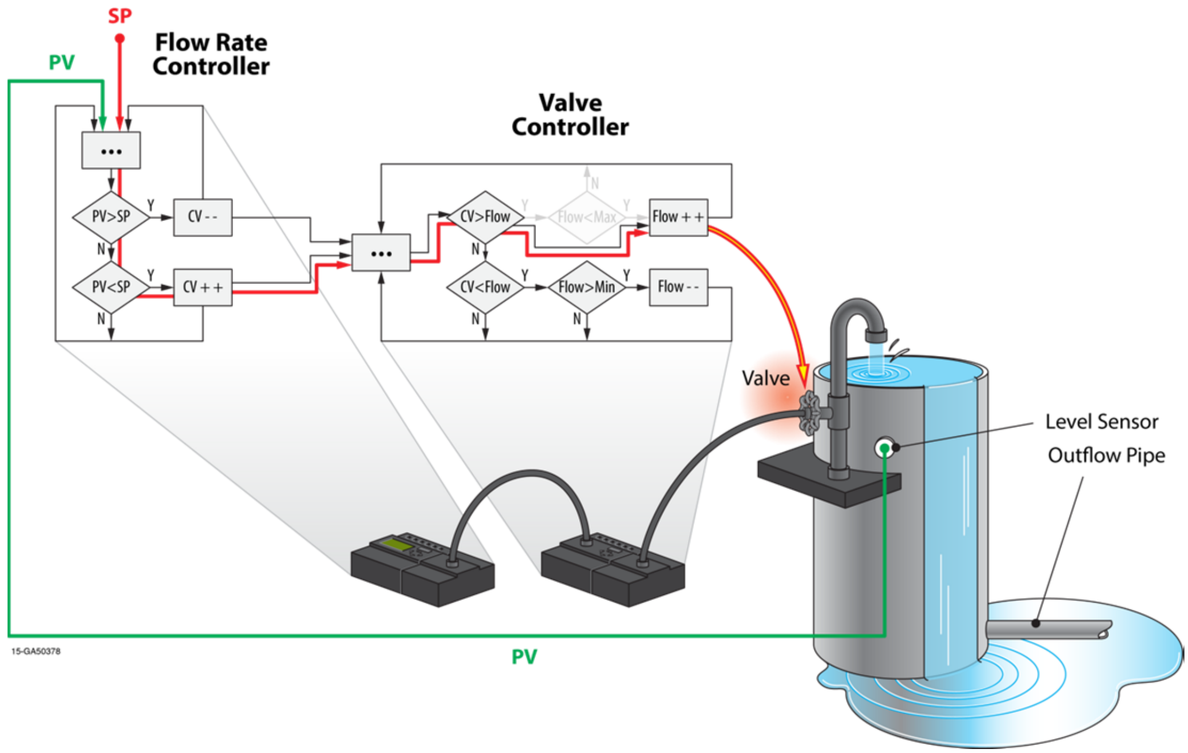


Figure 1. An ICS is a complex system composed of multiple layers of software applications and networked devices. Concolic execution for industrial control systems provides a methodology to discover bugs in such systems. For example, a bug in a critical flow loop is discovered by the analysis along the indicated red path through the logic of both devices' programs.

Benefits to DOE

This work will help to ensure the cybersecurity of critical energy infrastructure. In particular, this work will directly meet an objective of DOE's *Roadmap to Achieve Energy Deliver Systems Cybersecurity*, viz., to "Develop and Implement New Protective Measures to Reduce Risk." In addition, Presidential Policy Directive 21, "Critical Infrastructure Security and Resilience," recognized the need to advance R&D for methodologies to enable a more resilient critical infrastructure.

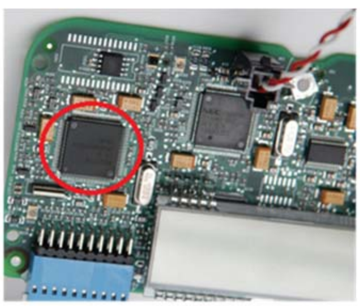
15-097—Security Risks Posed by Convergent Evolution in Industrial Control Systems Internals

Virginia Wright, Josh Hammond, Andrew VanVleet, and James Gibb

This project investigated the hardware components and code used in control-system internals to determine if market forces are pushing unrelated vendors to adapt common components and solutions. This project refers to this use of common internal components as "convergent evolution," borrowing from biology the concept that disparate species in a shared ecosystem tend to adapt similar features in response to common environmental drivers. Factors driving potential convergence in the control system industry include the costs of designing and maintaining multiple unique hardware components, the growing availability of common commercial libraries, and the desire to design solutions that are applicable to many industries and applications.

Summary

This project created a catalog of the hardware components of four smart meters from three distinct vendors and discovered that two of the meters used two sets of comparable chips, while two were completely different from the rest, or were "nonconvergent" (Figure 1).



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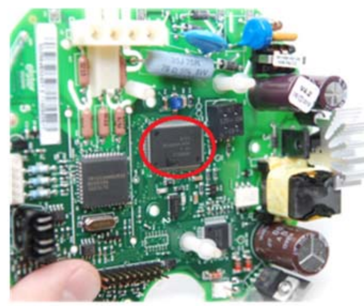
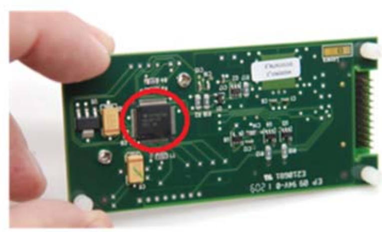


Company 2, Meter 1: Renesas M16C M30626FJPFP C U3 2130800

Company 1, Meter 1: TI 2AAN5PWG4 M430F135 REV N



Company 2, Meter 1: TI 15CF83TG4 M430F147 REV AA

Figure 1. Two identical chips found in two meters examined.

While these results suggest convergence could be occurring in the smart-meter market, they are not conclusive. Further study is required to determine how widespread the trend might be.

This project found the lack of convergence in two meters to be notable. If convergence becomes a significant trend, identification of nonconvergent products will be help stakeholders make decisions about risk mitigation.

Following the study of smart meters, seven programmable logic controllers (PLCs) were acquired, and their components were analyzed for evidence of convergence. No common hardware components were found between products from different vendors, which could be explained by the age of the PLCs studied. The PLCs involved were all older models from other INL projects.

The market forces believed to be pushing convergence have strengthened in the past few years. The lack of convergence in the older models could be consistent with the project hypothesis, but further exploration is needed.

While the exploration into convergence of PLCs was not conclusive, evidence was discovered suggesting that it is likely occurring.

Benefits to DOE

This research will further INL's predominance as a thought leader in ICS resilience and cybersecurity. This research offers both an opportunity for furthering academic work in resilient and fault-tolerant systems and operational work in measuring and mitigating ICS vulnerabilities. Both the Department of Homeland Security's ICS certification program and the INL's Mission Support Center have expressed an interest in the capabilities this research would create. DOE-NE may also be interested in sector-specific results for the energy sector.

15-098—Developing and Demonstrating Cost-Effective Ballistic Protection for Critical Electrical Assets

Todd L. Johnson, Henry S. Chu, Michael Bakas, James W. Schondel, and Benjamin Langhorst

The purpose of the project was to develop and demonstrate a prototype protective barrier to be used as a passive defense against ballistic threats to critical high-valued electrical assets. Recent events have demonstrated concerns and the need for protection of the nation's critical electrical infrastructure to ensure energy security. To mitigate these concerns, a full-scale protective barrier system, patent pending, was developed, and its protective levels were validated in live-fire tests.

Summary

The design of the passive protective barrier was intended to be modular for ease of installation, and the barriers were arrayed next to each other for flexibility in the barrier arrangement and protection strategies.

The design includes an A-frame structure that supports two armor cassettes and an optional top structure that extends the protective height by four feet and houses a single armor cassette (Figure 1). Each armor cassette supports a series of specially designed armor panels that can be replaced as needed. This design not only allows for the replacement of existing armor that may be damaged but also allows for flexibility in protection level as materials advance or requirements change due to various threats.

A demonstration of the ease of assembly was performed by a crew of electrical linemen who were not involved in the design or the construction of the prototype. Provided with just the assembly drawing, they were able to assemble and install the prototype in front of a transformer in approximately one hour, excluding a pre-job safety briefing (Figure 2).

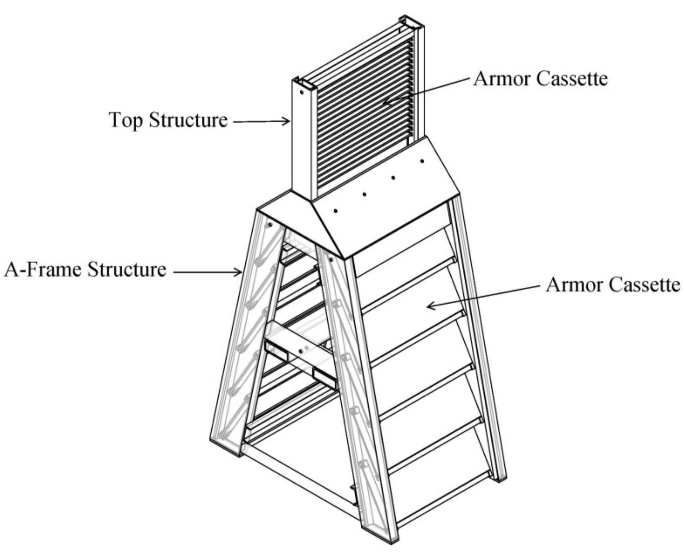


Figure 1. Isometric drawing of protective barrier.

Figure 2. Photograph of assembled protective barrier.

Ballistic testing at the National and Homeland Security Test Range validated that the design can mitigate all the highest threat categories listed under NIJ 0108 and UL 752 standards.

Benefits to DOE

This project provides a technical solution to a future requirement to protect our energy sector's critical infrastructure to ensure no interruptions to the U.S. energy supply. The demonstrated solution is modular, reconfigurable, and upgradable as threat types and attack methods evolve in the future. This barrier system has the potential to be adapted to provide ballistic, vehicle-ramming, and blast protection for guard posts and base entrances.

Presentations

Chu, Henry and Scott McBride, "INL Ballistic Barrier for Transformer Substation," Third Annual Power Grid Resilience Summit, San Diego, California, September 1, 2015.

Patents

Chu, Henry, Michael Bakas, Todd L. Johnson, and James Schondel, Protective Barriers and Related Methods, Attorney Docket No. 2939-P12966US (BA-869).

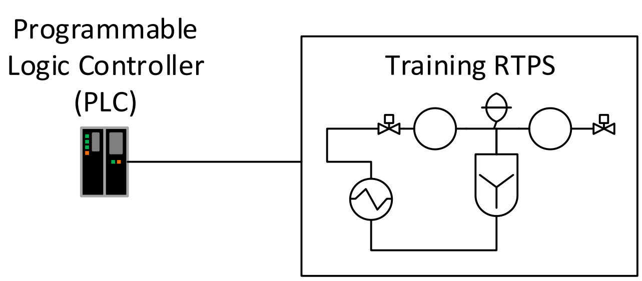
15-100—RTPS Real-Time Process Simulator

Jared Verba

The purpose of the Real-Time Process Simulator (RTPS) project is to generate a proof-of-concept simulation framework for industrial control systems (ICSs). This research is creating a more open and robust ICS remote input/output (IO) simulation framework for devices outside of the information technology network. This will enable current and future research efforts to produce more holistic and innovative cybersecurity solutions for ICS. By developing a field IO simulation framework that requires hardware in the loop for logic, researchers can examine solutions for protecting a system at the field-device level, such as for programmable logic controllers or remote terminal units. The side effects of this research will include better understanding and simulation of ICS proprietary protocols, devices, and sensors.

Summary

Research has produced two basic software components for simulation of an ICS. The primary component translates simulation data into a protocol that can be understood by a Siemens programmable logic controller. The second component provides an easy to expand Python programming simulation environment that feeds the primary component. This project will be demonstrated to future customers who are looking for a means to perform training on large ICS environments without the cost of physical equipment. This research is unique in that it uses current ICS hardware for process control and can be run with minimal resources. This research will also be loosely coupled with the current INL MOOSE and RELAP7 simulation software to create a proof-of-concept system geared toward nuclear cybersecurity. The end goal of this research is to create a proof-of-concept with direct applicability to the growing nuclear cyber business, current ICS training, and future security tools for ICS networks. Figures 1 and 2 show two examples of direct applicability for the proof-of-concept. The first area represents training system engineers and operators for cybersecurity events and how to handle them in a safe manner. The second area represents training nuclear operators and technicians how to respond to cybersecurity events in a nuclear environment. By using the RTPS coupled to hardware in the loop and existing nuclear simulations, a realistic and safe simulation of nuclear facilities can be achieved.



ICS Training facility

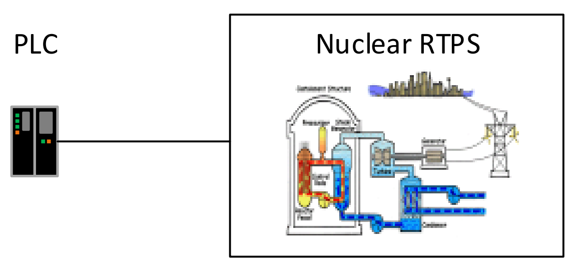
Benefits:

- Low Maintenance
- Fast reset of equipment
- Dynamic scenarios

Control over:

- Sensor degradation
- Equipment faults
- Network degradation

Figure 1. RTPS applied to common ICS security training.



Nuclear facility

Benefits:

- Low Maintenance
- Fast reset of equipment
- Dynamic scenarios
- Safe training methodology

Control over:

- Sensor degradation
- Equipment faults
- Network degradation

Figure 2. RTPS applied to cyber-nuclear scenarios for training.

Benefits to DOE

This research is directly applicable to the current and ongoing need for security in the industrial control system network. This project also meets a national need for enhanced security in the nuclear sector.

15-106—Automated Security Vulnerability Analyzer for Long-Term Evolution (LTE) Systems - LTE Hack Box

Kurt Derr, David Couch, and Sam Ramirez

Long-Term Evolution (LTE) is becoming the predominant cellular technology used by the Internet of Things, mobile communications, and the connected control systems within the interdependent critical U.S. infrastructure (smart grid, emergency response command and control, traffic control systems, etc.). As U.S. critical infrastructure relies more on communications between mobile devices, the cybersecurity of these LTE systems affects the security and resilience of critical U.S. assets, as well as public safety operations and emergency/disaster response.

In addition, software-defined radios (SDRs) are dramatically accelerating the pace of innovation and development of new radio technologies. Just as the personal computer ushered in a dramatic increase in the pace of software innovation, so the proliferation of SDRs is advancing wireless technologies. The powerful capabilities of inexpensive, easy-to-access SDRs are also allowing more prevalent, sophisticated attacks that would have previously required expensive equipment and highly skilled and knowledgeable people to perform.

Cyber vulnerabilities in a software system may introduce unmitigated attack pathways where threats may be exploited. Automated tools based on SDRs, especially for complex protocols such as LTE, are essential in order to identify these vulnerabilities, suggest mechanisms for mitigating those vulnerabilities to equipment providers, and improve the security of LTE. The objective of this R&D is to build an automated security-vulnerability analyzer tool, known as Hack Box, for LTE systems. Hack Box will discover vulnerabilities, demonstrate an exploit, and, if available, identify mitigations.

Summary

Within the first year of this project (FY 2015), a Hack Box prototype was developed that can be used to rapidly identify, experiment with, and characterize vulnerabilities in LTE systems. The test configuration consists of an SDR integrated with open-source LTE software. This combination creates a working fourth-generation cellular base station that is compatible with user equipment, such as a smart phone, tablet, or computer. The prototype provides a platform for experimentation with LTE end-user and asset-owner equipment. With further development, the prototype could be used to discover vulnerabilities and demonstrate exploits in commercial off-the-shelf LTE systems utilized by the general public and government personnel, thereby resulting in opportunities to conduct vulnerability and mitigation-solution research with multiple providers of such equipment. The prototype provides a rogue-cell-tower and base-station capability that can be used for vulnerability discovery and mitigation for public safety communications.

Essentially, this tool replicates the applications and baseband processors within mobile phones and a base station on a general-purpose computer with an SDR. The baseband processor implements the LTE communications protocols that are responsible for all LTE cellular communications, and an LTE base station is also a processor that implements the LTE communications protocols. Through this replication, researchers can modify the code to exploit vulnerabilities in LTE mobile phones and LTE base stations.

This important tool allows INL researchers to view all data transfers at all levels of the "communications stack" (i.e., the set of network protocol layers that work together). Although many other organizations have a capability to connect LTE user equipment to the Internet, INL is one of few that can trace every bit through every part of the system. This tool could prove to be a very important milestone to further develop new tools that improve security and mitigate system threats.

Benefits to DOE

Cellular communication is playing an increasing role in the U.S. energy infrastructure, such as the smart grid. This research contributes to DOE's mission to advance energy and homeland security in the United States by enhancing the security and resilience of energy infrastructure through the R&D of methods to identify and mitigate cybersecurity vulnerabilities within mobile communications. This science and energy research focuses on emerging and current communications technologies that are becoming prevalent within the energy, and other critical, infrastructure sectors.

Furthermore, the experimental capability to discover vulnerabilities in commercial off-the-shelf LTE systems and devices would greatly increase the cybersecurity of public safety and emergency response communications being implemented through the National Public Safety Broadband Network by the First Responder Network Authority.

15-107—Advanced Visualization for Simulation and Modeling

Scott J. Thompson and Matthew T. Kinlaw

For nonproliferation-focused detection applications, Monte Carlo N-Particle (MCNP6) is currently the modeling tool of choice due to its long history of benchmarking and seamless integration with supercomputer environments (such as INL's High-Performance Computing resources). However, a key component of any simulation and modeling work that MCNP6 fails to address is communication of problems through visual media. The code itself has low-level, two-dimensional, geometry-plotting capabilities, but these are designed for debugging and not for communication purposes. The objective of this project is to develop a visualization package that is capable of reading MCNP6 input files directly and producing visual media suitable for communication in journal articles, proposals, and presentations. To accomplish this objective, the project seeks to provide a tool for researchers with the following capabilities:

- Fully customizable, high-resolution, three-dimensional renderings
- Real-time particle track visualization
- The ability to create videos
- Integration with Microsoft's KINECT Version 2 sensor.

Summary

FY 2015 efforts have focused on building the fundamental algorithms necessary for development of a final product. These efforts have included several areas of emphasis. The first is the development of the code necessary to read an MCNP6 input file and translate it into a mesh geometry that is usable by Microsoft's Direct3D application programming interface. At the current stage, the code is able to interpret geometries composed singularly of macrobodies for mesh conversion.

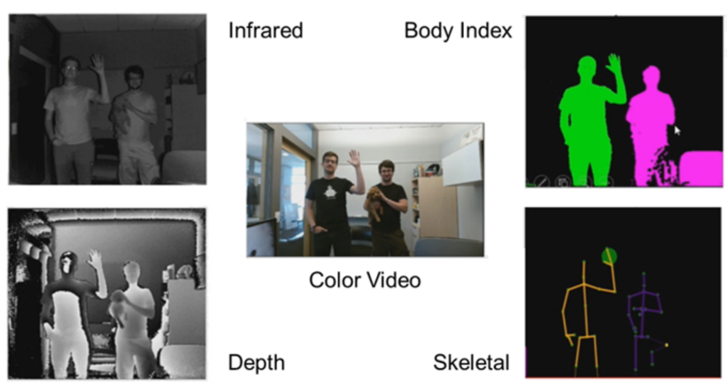


Figure 1. Images taken from the Microsoft KINECT website demonstrating the various data streams the sensor provides. Not shown is the direction-sensitive audio stream.

The second area is the development of the tool's user interface. Design work has been initiated for a user-controlled plotting window with the ability to adjust various characteristics of the rendered geometry, including individual surface color and textures, lighting, and component transparency. MCNP6 has a user option to produce what is called a PTRAC file that includes a variety of physical information about a particle's movement, including its position, at each interaction point in the geometry. An algorithm to interpret these data has been developed so that the user will have the option to visualize the particle's movement in the rendered geometry. The final area of work in FY 2015 has been regarding the integration of Microsoft's KINECT Version 2 sensor. This sensor provides six different information streams that include standard color camera video (1920 × 1080 @ 30 frames per second), infrared video, time-of-flight depth sensing, direction-sensitive audio, human-body identification (up to six individuals), and the ability to track up to 26 skeletal joint positions per identified body, all in a 70-degree horizontal field of view. Figure 1 is a graphic from Microsoft demonstrating the various data streams. The initial goal will be to incorporate gesture recognition into the tool's interface for state-of-the-art presentation capabilities.

Benefits to DOE

Simulation and modeling make up a fundamental component of almost every research project across all mission spaces. For nonproliferation and counterproliferation work within DOE and National Nuclear Security Administration focused on the development of material detection and characterization systems, the developed tool will aid in the communication of problems and ideas that naturally arise during and after the research process. The tool will directly help nonproliferation researchers by increasing the quality of future publications, presentations, and proposals. The INL capabilities gained through the development of this tool with regard to the KINECT Version 2 sensor have the potential for application to nonproliferation, counterproliferation, and first-responder mission spaces.

15-111—Adversary Signature Development and Threat Analysis

Sarah Freeman and Katya Le Blanc

Cybersecurity is most effective before an attack. However, the development of adequate proactive protection remains a challenge. Recent years have seen an explosion of threat-focused research aiming to meet the needs of an ever-evolving cyber landscape. Organizations, both public and private, have sought to advance threat analysis processes, methodologies, and capabilities in order to improve capabilities and training for the next generation of defenders. This research will improve the understanding of the cyber community by developing additional structured analytical techniques and a corresponding model to address the current challenges facing complex threat analysis.

Summary

This research blends the current concepts of behavioral economics with the analytical procedures used in law enforcement and the intelligence community in order to fill the current gap in threat analysis capabilities. The goal of this work is greater understanding of how hackers interact, share information, approach problems, and use technology. Central to this process is the development of a model that more fully describes attack scenarios and campaigns. The model is supported by a collection of indicators (such as exploits and malware used), which serve as the basis for attribution. The research conducted during FY 2015 covered two related but uniquely focused phases for the identification, development, and verification of a new collection of indicators. The data collected from these two phases have been combined into a single model, which will serve as a library of information for the development of cyber adversary profiles (see Figure 1).

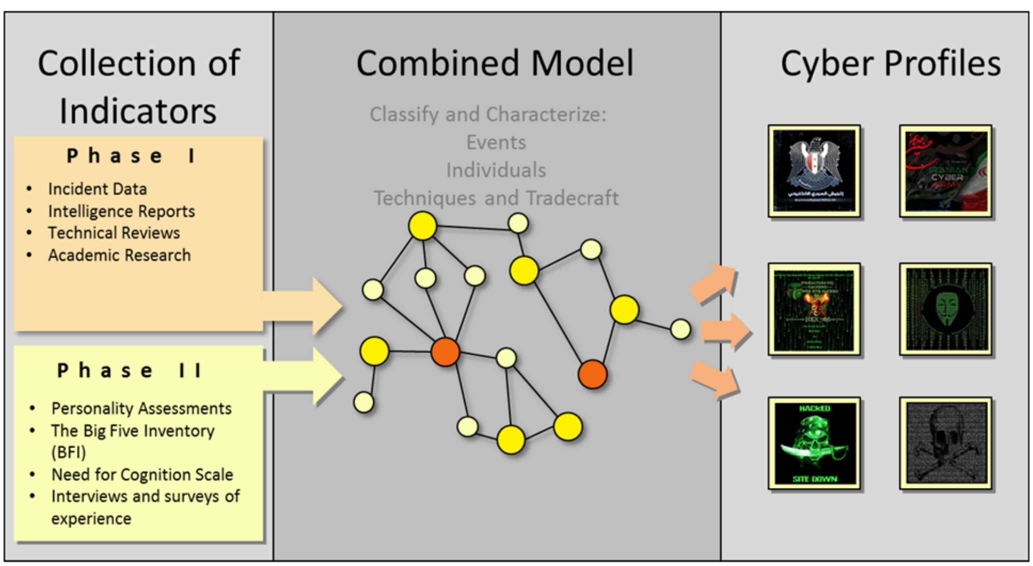


Figure 1. The experimental design was constructed to include both objective and subjective indicators for ontology development. This model then serves as the analytic framework for the creation of cyber profiles.

An evaluation of the existing research determined that most of it focused on the motivations, learning styles, and approaches of cyber researchers. Unfortunately, the majority of this work also revealed a pervasive bias that limited understanding of the group. To develop a more accurate representation of the cybersecurity community, this research incorporated qualitative data sets composed of structured interviews, peer evaluations, incident data, and cyber intelligence reports from actual events.

A critical component of Phase I included the development and analysis of cyber incidents. The goal of this process was two-fold. First, it ensured that a wider perspective was considered for both this research and the development of the combined model because it was assumed that the cyber researcher participants were not representative of the complete hacker culture. Second, post-mortem analysis of cyber incidents assisted with the aggregation of "typical" indicators, that is, the components most often tracked and recorded following a cyber incident. The experimental design for Phase II included two vetted psychological assessment tools (the Need for Cognition Scale and the Big Five Inventory), as well as an INL-designed structured interview protocol to investigate the experiences, skills, and technology preferences of the cybersecurity community.

By expanding the quantitative data beyond those that are traditionally collected post-incident, the research team was able develop a more comprehensive view of the personal motivations and thought processes of these individuals. By the same token, the inclusion of cyber-incident data allowed the research team to evolve the ontology further than would be possible with the interviews alone, especially given the size of the potential sample pool. The end result of this holistic approach is a more comprehensive view of potential signature components that can be expanded in the future.

Benefits to DOE

This research contributes directly to DOE's goal of securing critical infrastructure from cyber attacks by evaluating the existing cyber-researcher community's methods and capabilities. This novel threat-analysis approach will allow organizations to more accurately characterize individuals who pose modern cyber threats, therefore promoting the creation of evolved systems to protect industrial control systems.

Presentations

Freeman, S., "Adversary Signature Development and Threat Analysis," Early Career Researcher Symposium, INL, July 30, 2015.

APPENDIX

Benefiting Agencies

APPENDIX

Benefiting Agencies

The following table provides a listing of individual LDRD project contributions to each benefiting agency. In addition, FY 2015 total investments are provided for each benefiting agency.

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
13-011	Deborah T. Newby	Integrated Approach to Algal Biofuel, Biopower, and Agricultural Waste Management					•					•
13-013	S. Bulent Biner	Development of a Micromechanistic Phase-Field Modeling Approach for the Life Estimation and Risk Assessment of Reactor Pressure Vessels							•			•
13-027	Eric J. Dufek	Diagnostics of Advanced Energy Storage Materials					•			•		•
13-029	A. Joe Palmer	In-Pile Detection of Crack Growth in the ATR	•		•				•			•
13-032	Mark Carroll	Experimental and Computational Analysis of Hydride Microstructures in Zirconium in Dry Storage Conditions							•	•	•	•
13-033	Leigh R. Martin	Magnetic Separation Nanotechnology for Spent Nuclear Fuel Recycle		•					•			•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
13-035	Ken Bateman	Development of New Molten Salt Sensor Technology for Application to Safeguarding Pyroprocessing	•	•	•				•			•
13-039	Gary S. Groenewold	Induction-Based Fluidics Mass Spectrometry for Characterizing Radioactive Extraction Solvents							•	•	•	•
13-050	Yongfeng Zhang	Concurrent Atomistic to Macroscale Modeling of Materials under Irradiation Using the Phase Field Crystal Method	•		•				•	•	•	•
13-060	James E. Delmore	Metal Fluoride Preparation for AMS Analysis	•	•	•				•	•		•
13-065	Humberto E. Garcia	Multi-Domain Modeling, Simulation, and Integration Tools for the Dynamic Analysis and Optimization of Hybrid Energy Systems				•	•	•	•	•		•
13-068	Mitchell Plummer	Cooling in Fractured Geothermal Reservoirs: Analyses of Long-Term Cooling in Typical Geothermal Reservoirs and Application to Geothermal Resource Potential					•			•		•
13-071	Benjamin Spencer	Advanced Fracture Modeling for Nuclear Fuel							•			•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
13-079	Dayna L. Daubaras	Diverse Biological Factories for Sustainable Manufacturing					•			•		•
13-092	Jana Pfeiffer	Fission Product Standard Production	•	•	•				•		•	•
13-093	Hussein Moradi	Spectrum Allocation and Communications in Dynamic Spectrum Access Channels	•	•	•	•			•	•	•	•
13-095	Robert Youngblood	Development and Validation of a Societal Risk Goal for Nuclear Power Plant Safety			•				•		•	
13-097	Derek Gaston	MOOSE Capability Extension in Support of Full-Core Modeling	•		•				•	•	•	•
13-105	Jian Gan	Micro/Nano Scale AFM-Based Thermal Conductivity Measurement and Atomistic Modeling for Oxide Fuel: The Effects of Grain Boundary, Fission Gas, and Radiation Damage							•	•		
13-106	Peter Zalupski	Building Organic-Inorganic Hybrid Materials to Protect Metal Ion Sequestering Agents from Radiation-Induced Oxidative Damage	•		•				•		•	•
13-110	Humberto E. Garcia	Nuclear-Renewable-Oil Shale Hybrid Energy System				•	•	•	•			

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
13-115	Mark DeHart	Multi-Scale Full-Core Reactor Physics Simulation of the Advanced Test Reactor			•				•			
13-118	Shawn West	Geomagnetic Disturbance Field Coupling Measurements on INL Power Grid	•	•	•	•					•	•
13-121	J. Keith Jewell	Advanced In Situ Measurement Techniques in TREAT	•	•	•				•	•	•	•
14-009	James E. O'Brien	Development of an INL Capability for High-Temperature Flow, Heat Transfer, and Thermal Energy Storage with Applications in Advanced Small Modular Reactors, High-Temperature Heat Exchangers, Hybrid Energy Systems, and Dynamic Grid Energy Storage Concepts				•	•		•			•
14-010	Darrell Knudson	Use of Linear Variable Differential Transformer (LVDT)-Based Methods to Detect Real-Time Geometry Changes during Irradiation Testing	•		•				•			•
14-025	Mitchell Greenhalgh	Minor Actinide and Lanthanide Separations in Alternative Media	•						•	•	•	•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
14-026	Yongfeng Zhang	Multiscale Modeling on Delayed Hydride Cracking in Zirconium: Hydrogen Transport and Hydride Nucleation							•	•	•	•
14-031	Richard Williamson	Multidimensional Multiphysics Modeling of Fuel Behavior during Accident Conditions							•			•
14-032	Jonathan Chugg	CAN Bus Security across Multi-Sector Platforms	•	•	•	•	•		•		•	•
14-035	Michael Daniels	Safer Energetic Materials – Ignition Prevention with Improper Heating Rate	•		•					•	•	•
14-036	David L. Chichester	Innovative Research for Fieldable Nuclear Measurements	•	•	•				•	•	•	•
14-037	David L. Chichester	Development of Advanced Nuclear Material Characterization Technology for Security Applications	•	•	•				•	•	•	•
14-038	Curtis Smith	Multivariate Calibration of Complex Simulation Codes Using Disparate Types of Evidence: Advanced Automated Validation of Modeling and Simulation Tools			•		•		•			

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
14-041	Paul A. Lessing	Uranium Nitride-Uranium Silicide Composite Ceramic Fuel Production via Spark Plasma Sintering							•			•
14-045	Scott J. Thompson	End-to-End Radiation Detector Enhancements for Improved Safety and Security in Safeguarded Facilities	•	•	•				•	•	•	•
14-075	Christian Rabiti	Development of Tools and Methodologies for Uncertainty Quantification and Validation for Multiphysics Fuel Performance Simulation							•			•
14-078	Subhashish Meher	Extended Stability Gamma-Gamma Prime Containing Nickel-Base Alloys				•	•	•	•			•
14-079	Aaron D. Wilson	Second-Generation Switchable Polarity Solvent Draw Solutes for Forward Osmosis	•				•	•	•	•	•	•
14-080	Dennis C. Kunerth	Battery Material Characterization Technologies					•					•
14-086	Kurt Myers	Development of a Microgrid/Smart Grid Test Bed for ESL and Super Lab Initiative, with Load Variability Characterization and Control for Renewable Energy Integration	•	•	•	•	•	•	•		•	•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
14-087	Thomas Lillo	Transparent Fiber Reinforcements for Transparent Protection Systems	•	•	•							•
14-091	Sergiy Sazhin	Battery Health Estimation Based on Self-Discharge Fast Measurement and Soft Short-Circuit Detection				•	•			•		•
14-093	Ryan Hruska	All Hazards Critical Infrastructure Knowledge Framework	•	•	•	•					•	•
14-094	Michael Bakas	SMC Advanced Armor Materials and Systems R&D	•	•	•	•				•		•
14-095	Gary S. Groenewold	In Situ Measurement of Electrolyte Chemistry in Battery Cells during Operation				•	•					•
14-098	Jian Gan	Irradiation Effects in Uranium Dioxide							•	•		•
14-104	Richard C. Martineau	Development of a Multiphysics Algorithm for Analyzing the Integrity of Nuclear Reactor Containment Vessels Subjected to Extreme Thermal and Overpressure Loading Conditions	•		•				•	•		•
14-106	Joshua J. Kane	Understanding the Growth of Ultra-Long Carbon Nanotubes	•			•	•		•		•	•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
15-002	Peter Zalupski	Experimental Scenarios of Adversity and Recovery in Aqueous Separations	•		•		•		•	•	•	•
15-013	Curtis Smith	Simulation-Based Analysis of Procedures and Accident-Management Guidelines							•			•
15-014	Darin Snyder	^{135}Cs Quantification: A ^{135}Xe Proxy	•		•				•		•	•
15-023	Justin Coleman	Development of Stochastic 3D Soil Response Capability in MOOSE to Provide Design and Beyond-Design-Basis Seismic Motions for Nuclear Facilities	•		•				•		•	•
15-032	Krzysztof Gofryk	Development of New Method for High-Temperature Thermal-Conductivity Measurements of Nuclear Materials							•	•		•
15-036	Craig Rieger	Resilience Metrics Design Establishing the Resilience Benefit of Smart Grid Advancements	•	•	•	•	•	•	•	•	•	•
15-039	Shannon M. Bragg-Sitton	Transient Modeling of Integrated Nuclear Energy Systems with Thermal Energy Storage and Component Aging and Preliminary Model Validation via Experiment				•	•	•	•			

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
15-040	Vivek Agarwal	Acoustic Telemetry Infrastructure for In-Pile ATR and TREAT Monitoring					•		•			•
15-060	Mark DeHart	Development of Efficient TREAT Modeling Capabilities with Graphite Data Improvement			•				•	•		
15-071	Leigh R. Martin	Determination of Used Fuel Burnup through Fluorimetry of Activation Products	•	•	•				•	•	•	•
15-082	Matthew T. Kinlaw	Advanced Fission-Chain and Multiplicity Analysis	•	•	•						•	•
15-083	Shane Cherry	Visualizing Highly Dense Geospatial Data	•	•			•			•		
15-086	Rita Foster	Grid Data Analytics Framework				•	•			•	•	•
15-094	Jay Disser	Evaluation and Demonstration of the Integration of Safeguards, Safety, and Security by Design (3SBD)	•		•				•		•	•
15-096	Craig Miles	End-to-End Dynamic Program Analysis for Industrial Control Systems with Concolic Execution	•	•		•			•	•	•	•
15-097	Virginia Wright	Security Risks Posed by Convergent Evolution in Industrial Control Systems Internals	•	•	•	•			•		•	•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
15-098	Todd L. Johnson	Developing and Demonstrating Cost-Effective Ballistic Protection for Critical Electrical Assets	•	•	•	•					•	•
15-100	Jared Verba	RTPS Real-Time Process Simulator	•	•	•	•	•		•		•	•
15-106	Kurt Derr	Automated Security Vulnerability Analyzer for Long-Term Evolution (LTE) Systems - LTE Hack Box	•	•		•				•	•	•
15-107	Scott J. Thompson	Advanced Visualization for Simulation and Modeling	•	•	•				•		•	•
15-111	Sarah Freeman	Adversary Signature Development and Threat Analysis	•	•	•	•	•		•	•	•	•
15-125	Eric J. Dufek	Phosphoranimines for Advanced Battery Applications				•	•			•		•
15-128	Hai Huang	Microstructural Evolution and Mesoscale-Coupled Flow-Reaction-Fracturing Processes in Organic-Rich Nanoporous Shales	•				•	•		•	•	•
15-135	Rob Hovsapian	Dynamic Simulations for Large-Scale Electric Power Networks in a Real-Time Environment Using Multiple RTDS				•	•		•	•		•

Tracking Number	Principal Investigator	Title	DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
15-140	Kevin L. Gering	Expanding the Utility of Advanced Chemical Physics Models for Electrolytes				•	•					•
15-141	Hongbin Zhang	Interfacing MOOSE Components to Enhance Capability			•				•			
15-142	Maria A. Okuniewski	New In-Core Neutron Diagnostics at the University of New Mexico							•			
15-143	Douglas Burns	Development of Bayesian Uncertainty Quantification Tools for Use in Complex Modeling and Simulation Code Validation	•		•				•			•
15-144	Shelly Li	Investigation of Sonication-Assisted Electrolytic Reduction of Used Oxide Fuel in Molten Salt	•						•		•	•
15-145	J. Keith Jewell	Advanced Neutron and X-Ray Imaging at TREAT	•		•	•			•	•		•
15-146	Rebecca Fushimi	Tailoring the Kinetic Function of a Surface through Electronic Effects of Nanoscale Architecture					•	•		•		•
15-147	Lucia M. Petkovic	Rare Earth Element Catalysts for Carbon-Based Chemicals					•	•		•		•
		PROJECT TOTALS:	**33**	**17**	**34**	**25**	**30**	**10**	**50**	**36**	**21**	**57**

TOTAL INVESTMENTS

DOD	DHS	NNSA	DOE-OE	DOE-EERE	DOE-FE	DOE-NE	DOE-SC	DOE-Other	OFA
$15,295,061	$6,658,380	$16,215,750	$11,769,585	$13,893,337	$5,618,202	$28,609,323	$19,107,759	$11,748,173	$31,357,691

NOTE: This table identifies which program/sponsor benefits from each of the LDRD projects. Project total exceeds 81 projects funded in FY 2015 because multiple beneficiaries per project are allowed. Project total funding exceeds the approximately $18M FY 2015 LDRD budget because multiple beneficiaries are allowed for each project.

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