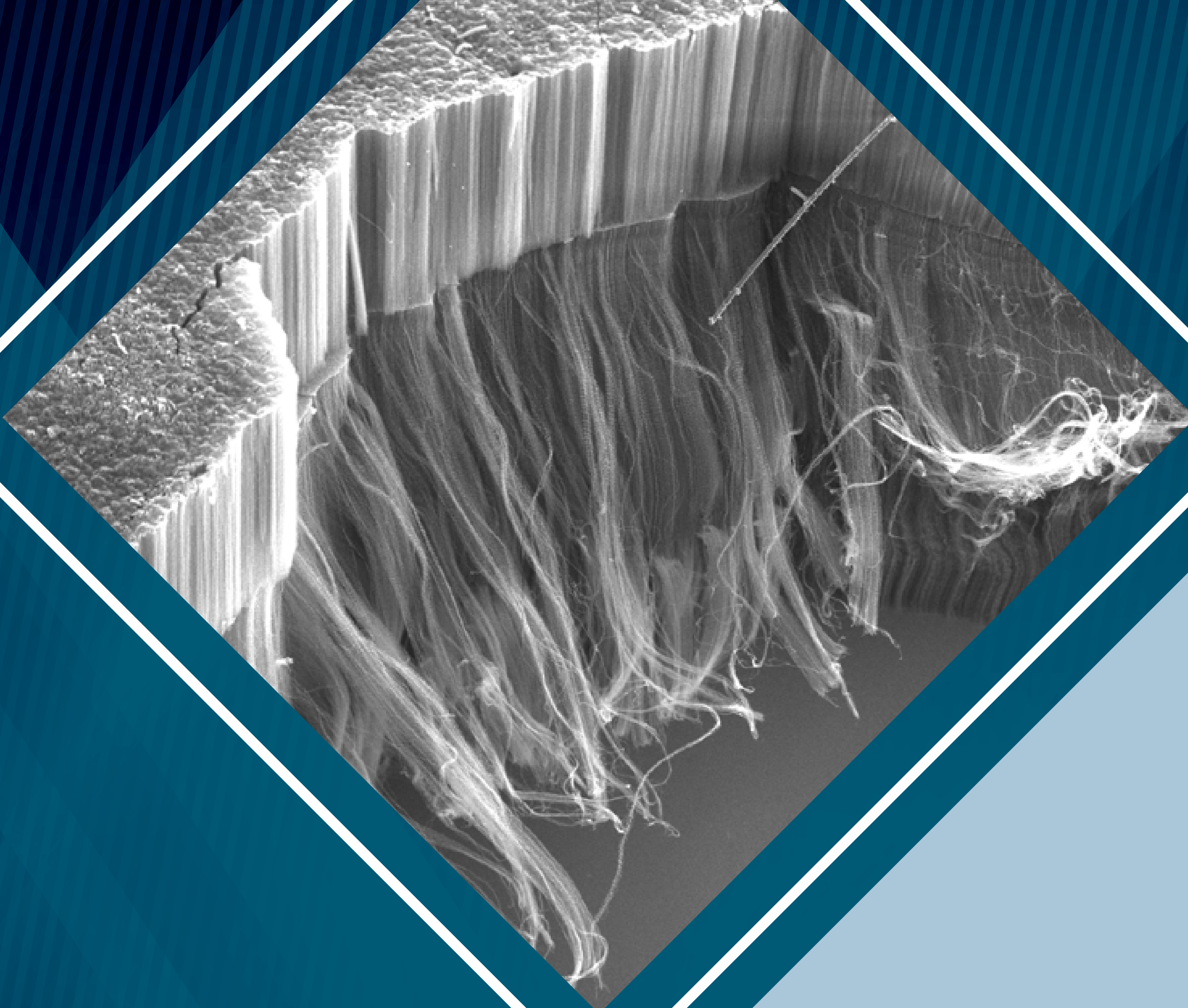
INL/EXT-18-52236

Laboratory Directed Research and Development Project Summaries

Projects Ending in Fiscal Year 2018

Idaho National Laboratory



INTRODUCTION

Congress designated Idaho National Laboratory (INL) as the nation's lead facility for nuclear energy research and development in 2005. In addition to our leadership in the core nuclear energy mission, INL has also become a world leader in national security and protecting critical infrastructure from manmade and natural threats.

Laboratory Directed Research and Development (LDRD) plays a vital role in helping INL fulfill its nuclear energy, broader clean energy and national security missions. INL's LDRD investments are focused on high-impact outcomes, modernizing and enhancing INL's core capabilities and recruiting some of the world's top science and technology (S&T) talent. INL's Laboratory Agenda and Annual Laboratory Plan are used to communicate the status of INL's core capabilities and our focus on strategic S&T initiatives for the future. To achieve the mission of INL and the Department of Energy (DOE), INL's LDRD is aligned with four strategic objectives: (1) advance nuclear energy, (2) advance hybrid energy systems, (3) advance design and manufacturing, and (4) develop critical national and homeland security capabilities. INL's ability to achieve these strategic objectives depends on the integration and application of our core capabilities in use-inspired basic and applied research and world-class capabilities. LDRD investments in scientific and engineering staff, postdocs, students and collaborations enable new science, technology and engineering capabilities. In collaboration with our university, industry and other national laboratory partners, LDRD investments help grow our scientific foundation and accelerate innovation and the development of solutions to energy and security challenges faced by the nation and globe.

The objectives of the LDRD program are to (1) maintain INL's scientific and technical vitality; (2) enhance INL's ability to address current and future DOE missions; (3) foster creativity and stimulate exploration of forefront areas of S&T; (4) serve as a proving ground for new research and development (R&D) concepts; and (5) support high-risk, potentially high-value R&D.

This report highlights projects that were completed in FY 2018. This report provides a brief summary of projects and the future technology innovations and cutting-edge research that our researchers are pursuing in order to shape the future of our energy supply and national security. The intent of the report is to acquaint our stakeholders with the LDRD program and give them an opportunity to experience the breadth of research and development at INL.

Inside, you will read about cutting-edge R&D that builds INL's core capabilities, aligns with INL's strategic plan and benefits both DOE and an expansive sponsor base consistent with DOE and INL missions. This R&D creates opportunities for our staff, attracts promising young scientists and engineers, and helps educate the next generation of researchers. Many LDRD projects support undergraduate and graduate students and enhance university and industry collaborations.

LDRD projects are selected on a competitive basis through rigorous peer-review and management processes, and these projects build a creative environment grounded in scientific and technical excellence.

Over the years, science and innovation resulting from LDRD projects have benefited INL in a variety of ways: new research programs; recognition through awards, publications and patented inventions; stronger scientific and engineering talent; and new tools, instruments and capabilities. The LDRD program is a key component of INL's ability to fulfill its nuclear energy, broader clean energy and national security missions and serve the American people.

Please take a few moments to read this report and learn more about the important work being done every day at Idaho's national laboratory.

This report includes posters presented at a poster session held August 30, 2018 at the Center for Advanced Energy Studies. At the session, a poster was presented for each Laboratory Directed Research and Development project ending in Fiscal Year 2018. A total of 33 posters were presented, and researchers shared their work with Idaho National Laboratory leadership and staff. Posters were judged by a cross-cutting group of senior researchers, and the top three posters were identified and are noted in this report.




PROJECT ID: 15-144

INL Initiative: Advance Nuclear Energy

Investigation of Ultrasound Assisted Electrolytic Reduction of Used Oxide Fuel in Molten Salt

Electrolytic reduction is an integral step in pyroprocessing to treat used light-water reactor fuels. The slow oxygen-ion diffusion through the used fuel particulates leads to low current efficiency, long operating hours, and re-oxidation of reduced metal fuels for the electrolytic reduction. The goal of this project was to understand the metal-oxide reduction mechanism and to improve the current efficiency of metal-oxide reduction. Sonication was applied to an electrochemical cell with molten lithium chloride-lithium oxide at 650°C, and the effect of sonication for improving the performance of electrolytic reduction of surrogate metal oxide, titanium dioxide or manganese dioxide was studied. This is applicable to the pyroprocessing of used fuels in oxide form by coupling ultrasound sonication with electrolytic reduction in molten Li_2O/LiCl. The principal investigator at Idaho National Laboratory and co-principal investigator at Center for Advanced Energy Studies have closely worked with the national technical director of Material Recovery and Waste Forms Development under the DOE Nuclear Technology Research and Development programs, and they are pursuing funding through that group.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Shelly Li

EXTERNAL COLLABORATOR (University of Idaho): Haiyan Zhao

Best graduate student poster presentation "Electrochemical Reduction of Metal Oxides in Molten Salt," TMS 147th Annual Meeting and Exhibition held in Phoenix, AZ, Mar. 2018

15-144 – Investigation of Ultrasound Assisted Electrolytic Reduction of Used Oxide Fuel in Molten Salt

Shelly Li (PI, INL) and Haiyan Zhao (co-PI, U of I)

Project Objectives

To understand the metal oxide reduction mechanism and to improve the current efficiency of metal oxide reduction which is applicable to the pyroprocessing of the used fuels in oxide form by coupling ultrasound sonication with electrolytic reduction in molten Li_2O/LiCl.

Technical Challenges

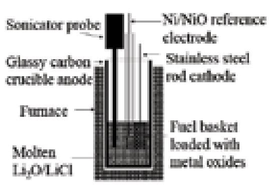
Low oxygen diffusion rate within the solid metal oxide for electrolytic reduction at high temperature molten salts leads to low current efficiency and long operation hours.

Approaches

- Quantitative product analysis using XRD Rietveld refinement;
- Coupling ultrasound with electrolytic reduction in high temperature molten salts.

Novelty

The sonication assisted electrolytic metal oxide reduction process is established within Argon glovebox and can continuously work up to 8 hours. The lift time of the sonicator probe is extended to 30 hours.



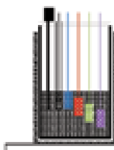
This project will expand expertise in the electrolytic reduction of used ligh water reactor (LWR) fuels for pyroprocessing and further establish the INL as a world leader in innovative fuel cycle technology. The achievement is also directly applicable to the projects for recycling rare earth elements under the Critical Material Institute (CMI).

Acknowledgement

Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

Results

-Project results



The effect of relative basket position

❖ Multistep reduction mechanism of TiO_2:

(1) $TiO_2 + 2Li^+ + O^{2-} \rightarrow Li_2TiO_3$ (fast);

(2) $Li^+ + e^- \rightarrow Li$;

(3) $Li_2TiO_3 + e^- \rightarrow LiTiO_2 + Li^+ + O^{2-}$ (fast) or

$Li_2TiO_3 + Li \rightarrow LiTiO_2 + 2\,Li^+ + O^{2-}$ (fast);

(4) $LiTiO_2 + Li \rightarrow TiOx$ ($x<1.5$) (Slow, the rate-limiting step)

❖ The effect of sonication on current efficiency:

(1) Increased reduction extent and current efficiency with sonication by 8% at over reduction potential;

(2) Larger improvement for under potential reductions with sonication increased by 38% for reduction extent and by 49% current efficiency;

(3) Higher reduction extent and current efficiency for a lower cathodic basket position.

-New Capabilities

❖ Oxides electrolytic reduction in molten salts at high temperature in CAES;

❖ Electrolytic reduction system coupled with sonication within argon glovebox

-Award

Best graduate student poster presentation "Electrochemical Reduction of Metal Oxides in Molten Salt", TMS 147th Annual Meeting and Exhibition (Phoenix, AZ) Mar. 2018

-Publications

- Meng Shi, Shelly Li, Haiyan Zhao. High Current Efficiency of NiO Electro - reduction in Molten Salt. *Journal of Electrochemical Society. Under 2nd round review*
- Meng Shi, Shelly Li, Haiyan Zhao. Electrolytic Reduction of Titanium Dioxide in Molten Li_2O/ LiCl. *Journal of Electrochemical Society. In preparation for submission to JECS*
- Meng Shi, Shelly Li, Haiyan Zhao. Study of Pseudo-reference Electrodes in Molten Li_2O/ LiCl Salts. *In preparation for submission to JECS*
- Meng Shi, Shelly Li, Haiyan Zhao. Sonication-assisted Electrolytic Reductions of TiO_2 in Molten Li_2O/ LiCl. *In preparation for submission to JECS*
- Meng Shi, Shelly Li, Haiyan Zhao. Effect of Electrodes and Salts Impurity on the Cyclic Voltammetry in Molten Li_2O/ LiCl. *ANS Transactions*, June, **2018**.
- Meng Shi, Shelly Li, Haiyan Zhao. Effect of Electrolyte Purity on Electrolytic Reduction of TiO_2. *ANS Transactions*, November, **2016**.

Please note that, due to space constraints, only select project products are included in this report. Publications that have been submitted for publication or which are under review are not included, nor are conference presentations.

PROJECT ID: 16-003

INL Initiative: Advance Nuclear Energy

Recycling of Tantalum-containing Waste Materials to Recover Tantalum Metal

Of late, recycling of recyclable materials and reclamation of strategic metals from their waste materials have assumed greater importance. The capability to be commercially deployed of a particular recycling method or strategy assumes even higher significance when the method or process can be developed as a generic technology to combine both secondary and primary manufacturing processes, as applicable, to the metal of interest. Tantalum is a strategic metal, and the U.S. currently does not have a primary tantalum manufacturer. The objective of this project was to establish the superiority of the direct oxide reduction process to prepare a variety of engineering materials (both metals and alloys) from their inexpensive oxide intermediates, either by the primary-production process or a secondary process by way of recycling of recyclable materials. In particular, this research included the development of a molten–salt-based electrochemical process for the reclamation of tantalum from its recyclable sources. Synthetic tantalum oxide waste materials were used to understand their refining behavior. This project resulted in several discoveries, including development of a new manufacturing process for tantalum-titanium alloys (used in the biomedical industry) and of a new concept to fabricate reference-electrode materials. Industry has shown interest in the results of this project.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Prabhat Tripathy

INTERNAL COLLABORATOR (Idaho National Laboratory): Mike Shaltry

EXTERNAL COLLABORATOR (Montana Tech of the University of Montana): Jerome Downey

DISSERTATION:

Chorney, M. P., *Investigations on Solid-State Sintering Behavior of Binary Refractory Metal Oxide Systems*, INL/MIS-18-45288, M.S. Dissertation, Montana Tech of the University of Montana, Spring 2018, Montana Tech Library, pp. 343.

PATENTS:

First filing: Prabhat K. Tripathy, "Electrochemical Cells for Direct Oxide Reduction and Related Methods," USPTO (non-provisional) application, US15/886041, filing date: February 02 2018.

NUMBER OF INVENTION DISCLOSURE REPORTS: 7

LDRD Project ID: 16-003(ANE)

Recycling of Tantalum-containing Waste Materials to Recover Tantalum Metal

PI: Prabhat Tripathy (INL), Mike Shaltry (Co-PI, INL) and Jerome Downey (Co-PI, Montana Tech of the University of Montana, Butte)

Motivators:

- Tantalum (Ta) is a strategic element (US DoD). No US-based Ta manufacturing industries currently exists.
- Recycling of Ta-wastes can serve twin purposes: less import and addition of value from wastes.

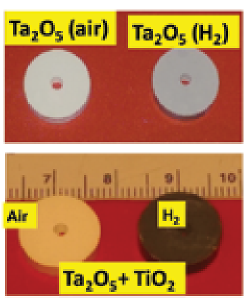
Objectives: (1) Tantalum Oxide (Ta_2O_5) and Mixed oxides containing Ta_2O_5 (Ta_2O_5+TiO_2; Ta_2O_5+HfO_2; Ta_2O_5+Nb_2O_5 and Ta_2O_5+WO_3) were the feed stocks for experimental research (2) optimized process conditions to prepare electrolytic grade Ta and its alloys and (3) examined its potential application(s) to refine two oxidized (commercially important alloys (nickel-titanium and titanium-aluminum-vanadium – additional work incorporated in the existing project scope).

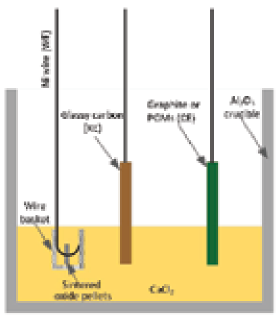
Technical Challenge: As recycling schemes for Ta-containing wastes (super alloys, waste Ta alloys) are being pursued/developed in industry, these companies refused to provide us some of their scrap materials. This was not a huge challenge as most of these scraps are oxidized (partially or completely) materials containing Ta and other metals. We used synthetic waste materials to understand their refining behavior.

Approach: (1) Preparation and characterization of oxide precursors (2) Electrochemical reduction of oxide/mixed oxide precursors and (3) Product analyses (XRD, SEM-EDS, residual oxygen measurement)

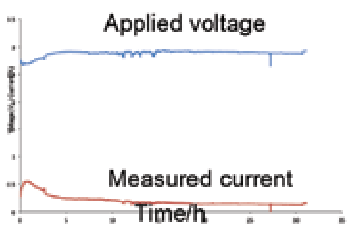
Experimental: (1) Preparation of the green pellets and (2) Sintering of the pellets (air/Ar-H_2 mixture) (3) Evaluation and characterization of the sintered pellets (porosity, morphology and phase analysis) (4) Electrochemical reduction (LiCl-Li_2O and $CaCl_2$-CaO systems) and (5) Product analyses (XRD, SEM-EDS, residual oxygen measurement).

- Electrochemical cell is the heart of the experimental unit/work.
- Although reduction experiments were performed in an argon atmosphere glove box, scale up work can be performed in a gas-tight arrangement outside a glove box environment.
- Three-electrode set up was used for the reduction experiments (oxide – working electrode; graphite/platinum group metal – anode; and glassy carbon – reference electrode).
- Reduction experiments were monitored by varying time, temperature, electrolyte compositions, anode materials and sintering oxides prepared under two different atmospheres: air and H_2).

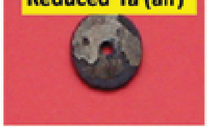




Electrochemical Reduction cell



No thinning of ruthenium anode



Reduced Ta (air)

Ta-Ti Powder

Research Novelties

- ✓ Oxide precursors prepared in H_2 showed better products (unreported).
- ✓ Defects in the oxide/non-stoichiometry is the key to achieve good reducibility (unreported).
- ✓ Developed new anode materials to elevate the status of the developed process to the elite club "green technology".
- ✓ Electrolytic grade Ta powder (>99% pure) could be prepared in just one step.
- ✓ Reported new in situ high-temperature XRD data for the binary alloys.
- ✓ More insight into the understanding of the binary Ta-Hf system (unreported).
- ✓ Successfully developed a new manufacturing process for tantalum-titanium alloys, an important bio-medical material.
- ✓ Developed a new concept to fabricate new reference electrode materials for carrying out fundamental electrochemical measurements.
- ✓ Preliminary results to refine partially oxidized NiTi alloys show initial promise.

Results

- ✓ One non-provisional US patent filed (BA 971/US15-886041, filing date: Feb. 02, 2018).
- ✓ Three IDRs submitted (BA1008, BA1062 and BA1063). reducibility (unreported). One more being prepared.
- ✓ One published paper.
- ✓ One M.S. dissertation (Montana Tech, 2018).
- ✓ One conference participation (2017 TMS).
- ✓ Trained two students (one as INL summer intern and the other one at the MTech) in the field of materials chemistry.
- ✓ Five manuscripts being prepared for peer-reviewed publications.
- ✓ Diado Steel (Japan), Momentum Technology (US), Defense Logistic Agency shown interest in new anodes.
- ✓ A University of Utah Prof. is assisting to get us connected to a suitable industry (possibly Ta/ refractory metals).

PROJECT ID: 16-010

INL Initiative: Advance Nuclear Energy

Development of a Fully Coupled Radiation Damage Production and Evolution Simulation Capability

The aim of the proposed research was to develop and demonstrate a capability to simulate radiation damage within the Multiphysics Object Oriented Simulation Environment (MOOSE), finite-element framework, tightly coupled to neutronics calculations. This project developed a coupled simulation capability for radiation damage, which is a critical consideration for nuclear materials. This project produced a new model, with first-of-a-kind coupling for physics-based radiation sources and algorithms for the analysis of microstructures under irradiation. The results generated from this research are being used in an application in new Nuclear Energy Advanced Modeling and Simulation programmatic funding areas, and the principal investigators have identified program needs for dosimetrey in Nuclear Science User Facility programs.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Daniel Schwen

INTERNAL COLLABORATORS (Idaho National Laboratory): Sebastian Schunert, Yongfeng Zhang, Javier Ortensi

EXTERNAL COLLABORATOR (Virginia Polytechnic Institute and State University): Xianming Bai

PUBLICATIONS:

Zabriskie, A., S. Schunert, D. Schwen, J. Ortensi, B. Baker, Y. Wang, V. Laboure, M. DeHart, and W. Marcum, "A Coupled Multiscale Approach to TREAT LEU Feedback Modeling Using a Binary-Collision Monte-Carlo–Informed Heat Source," *Nuclear Science and Engineering* (2018), pp. 1–20.

Zhang, Y., D. Schwen, and X.-M. Bai, "Molecular dynamics simulations of concentration- dependent defect production in Fe-Cr and Fe-Cu alloys," *Journal of Applied Physics* 122 (2017), 225902.

LICENSES:

Schwen, Daniel, Yongfeng Zhang, Jason Hales, Javier Ortensi, Sebastian Schunert, Cody Permann, Derek Gaston, Brian Alger, and Andrew Slaughter. "MAGPIE: Mesoscale Atomistic Glue Program for Integrated Execution," CW-17-08 (software released as open source).

Advancing Nuclear Energy

16-010 Development of a fully coupled radiation damage production and evolution simulation capability

PI: D. Schwen, co-PIs: S. Schunert, L.K. Aagesen, A.M. Jokisaari, X. Bai (VT)

Objective

Goal: Native Moose application for **radiation damage**

Why is radiation damage **important** for nuclear materials?
- Changes material properties, e.g. therm. conductivity
- Swelling in nuclear materials
- Drivesdislocation, gas bubble formation
- Patterning, ballistic mixing, gas resolution

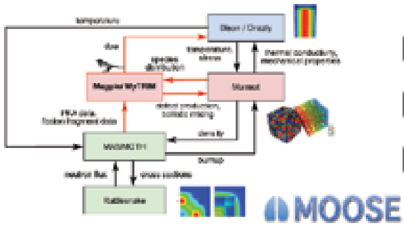
Magpie: a multiscale simulation code

10^{-9} m — Microstructure evolution Concurrent Marmot/Magpie

10^{-2} m — Engineering scale: dpa estimation Rattlesnake, NRT, Bison

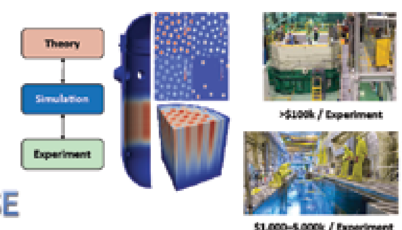
10^{-6} m — Microscale heat deposition Rattlesnake, Moose heat conduction

Fully Integrated Radiation Damage in Moose Ecosystem



Magpie Capabilities
- Concurrent coupling: neutronics, phase field, Monte-Carlo
  - Parallel Recoil Simulation ↔ Spatially decomposed FEM
- Reduced order models (ROM): fast re-solution, fast spatial heat deposition, polyatomic NRT

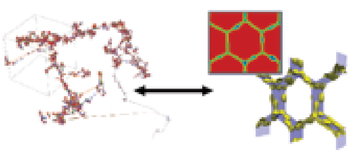
Impact on INL's R&D



Value proposition
- Help **design** experiments (reduce failed iterations)
- Help **understand** conditions
- Help **interpret** results (get more value out of the runs)

Challenges

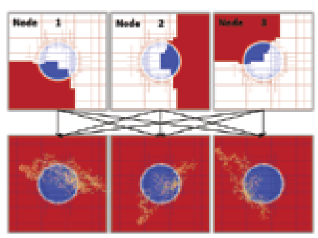
- Connecting vastly different simulation and parallelization paradigms



- Reduced order models for flexible fidelity and long length and time scales
- Bidirectional communication
  - Microstructure data influences scattering cross sections
  - Cascades feed back into mesoscale

Approach

- Magpiem as parallel communication hub and data manager



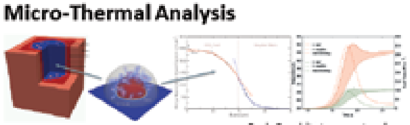
- Massive HPC scalability using MPI and threads

Novelty

- **First of a kind coupling** for physics based radiation sources
- MOOSE framework integration for **multiscale and multi-physics** coupling
- **Algorithms** for analysis of microstructures under irradiation
- Never before seen **fidelity** in
  - Spatially resolved **point defect** production in microstructures
  - Engineering scal **dosimetry** in complex compounds (DPA rates in alloys)
  - Spatially resolved **energy deposition**
- Novel **convolution based radiation ROM**

Results& Products

Micro-Thermal Analysis

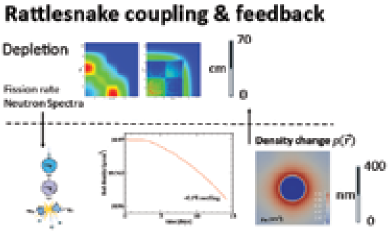


Transient Test Reactor (TREAT)

Fuel–Graphite temperature lag ΔT drives feedback of LEU core

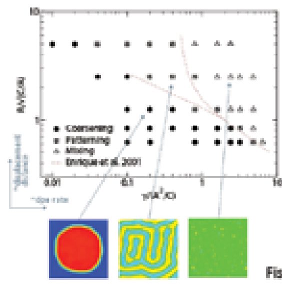
TREAT fuel: microscopic UO_2 grains. Magpie computes fission fragment transport. Important capability for LEU TREAT conversion M&S!

Rattlesnake coupling & feedback



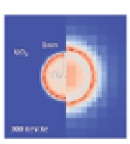
Phase Field (Grand Potential) & BCMC swelling

Microstructure under irradiation



Code verification

Ballistic mixing in competition with coarsening leads to **well understood** microstructure evolution. We **reproduce theoretical predictions.**



Fission gas resolution

Magpie (Open Source) GitHub

Mesoscale-Atomistic Glue code for Integrated Execution
- Couples BCMC to FEM
- Couples to Rattlesnake
- Full MPI & Thread parallelism
- FFT (microstructural analysis)
- Reduced Order Radiation Model

In Numbers

12372	Lines of Code
397	Commits
69	MOOSE Objects
54	Tests

Publications & Future

Publications & Presentatio
- Molecular dynamics simulations of concentration-dependent defect production in Fe-Cr and Fe-Cu alloys, Y. Zhang, D. Schwen, X.-M. Bai, J. Appl. Phys. 122 (2017) 225902.
- A Coupled Multi-scale Approach to TREAT LEU Modeling Using a Binary-Collision Monte-Carlo Informed Heat Source, A. Zabriskie et al., submitted to Nucl. Sc. & Eng.
- Evolution of Microstructures in Radiation Fields using a Coupled Binary-Collision Monte-Carlo Phase Field Approach, D. Schwen et al., in preparation for Comp. Mat. Sci.
- Heat Source Characterization in A TREAT Fuel Particle Using Coupled Neutronics Binary Collision Monte-Carlo Calculations, S. Schunert et al., Proceedings of the M&C 2017 conference, Jeju, Korea (2017).
- TMS 2017, San Diego, Talk: Coupling Radiation Damage from Binary Collision Monte Carlo to Phase Field Microstructure Evolution, D. Schwen, S. Schunert.
- MS&T 2016, Salt Lake City, Talk: Coupling Radiation Damage from Binary Collision Monte Carlo to Phase Field Microstructure Evolution, D. Schwen, S. Schunert.
- MMM 2016, Dijon, France, Talk: Coupling Radiation Damage from Binary Collision Monte Carlo to Phase Field Microstructure Evolution, D. Schwen, S. Schunert.
- TMS 2016, Nashville, Talk: Coupling Radiation Damage from Binary Collision Monte Carlo to Phase Field Microstructure Evolution, D. Schwen, S. Schunert.

Interns

2016
- Pedram Ghassemi, North Carolina State University

2017
- Marin Sessim, The Pennsylvania State University
- Ben Dacus, North Carolina State University
- Adam Zabriskie, Oregon State University

2018
- Amani Cheniour, University of Florida
- Daniel VanWasshenova, Idaho State University
- Adam Zabriskie, Oregon State University

Follow-on Funding
- Application in new NEAMS programmatic funding areas
- Identified program needs for dosimetry in NSUF program
- CASL/Bison engineering scale needs for dpa damage as model parameterization

PROJECT ID: 16-013

INL Initiative: Advance Nuclear Energy

Micromechanistic Modeling Approach for Quantitative Predictions of Delayed Hydride Cracking in Zirconium Alloys

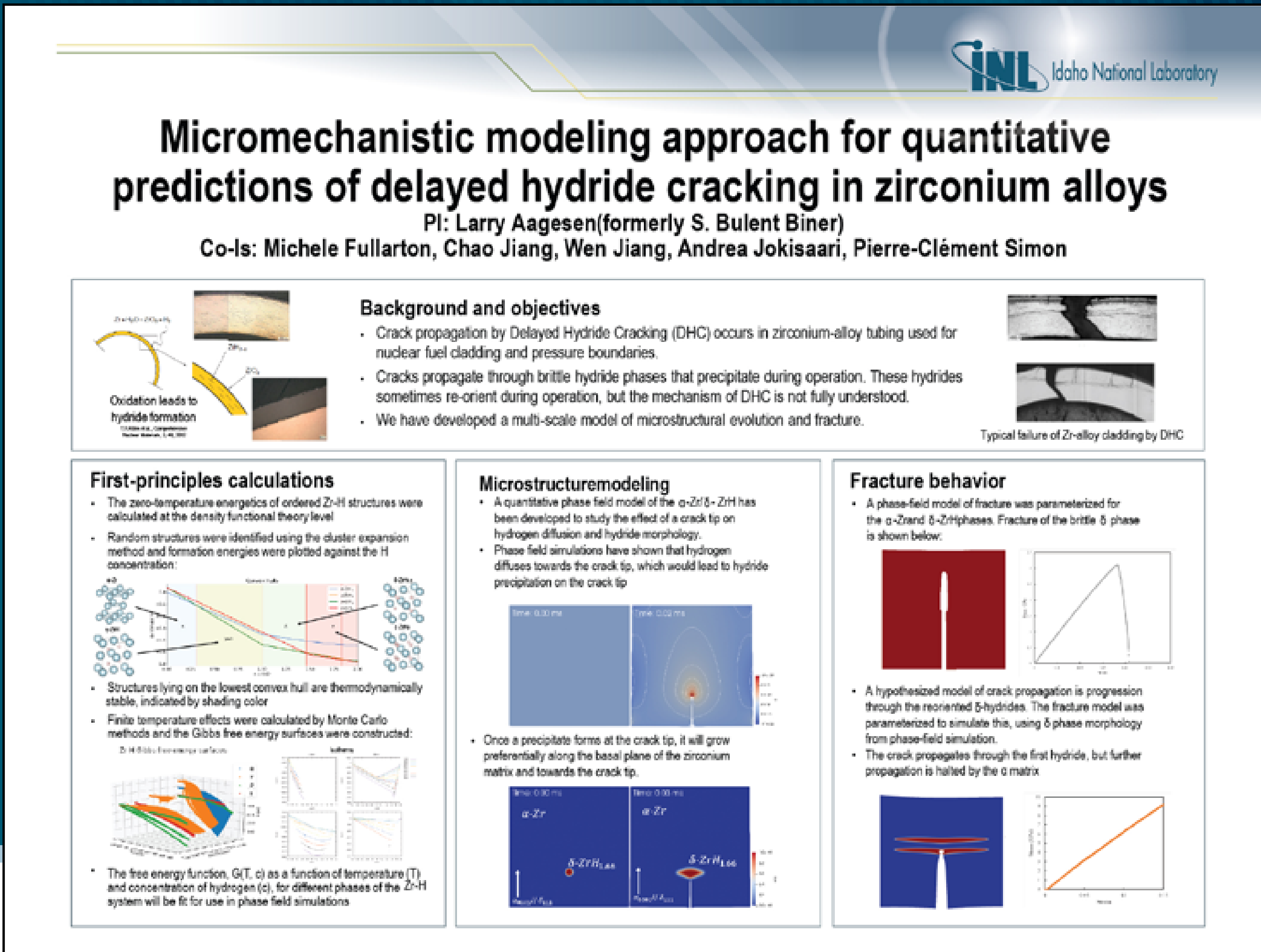
Zirconium alloys are excellent for use in fuel cladding and structural components in nuclear reactors; however, they are susceptible to two forms of hydrogen embrittlement: loss of fracture toughness and a stable, time-dependent crack growth mechanism, called delayed hydride cracking. The objective of this research was to develop a micromechanistic phase-field unified model. The model brings together coevolution of the hydride phases due to hydrogen transport and the mechanisms of crack growth resulting from brittle fracture of hydride phases and ductile fracture of the matrix. This framework enables quantitative prediction of delayed hydride cracking under transient conditions. This approach was the first of its kind to directly address issues associated with fuel performance and long-term storage based on fundamentals of microstructural evolution and fracture. A hypothesized model of crack propagation is progression of the cracks through reoriented δ-hydrides and the surrounding α matrix phase that separates the hydrides by small distances. However, the model showed that the cracks cannot propagate through the α matrix due to its fracture toughness, even for very close δ-hydride spacing. Instead, a more likely mechanism of crack propagation is growth of existing δ-hydride particles toward the crack tip. The models will be employed in the DOE - funded Integrated Research Project FC-1: Modeling of Spent Fuel Cladding in Storage and Transportation Environments. The developments resulting from this proposal are also applicable to other hydriding alloy systems, such as titanium and lithium.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Larry Aagesen (formerly Bulent Biner)

INTERNAL COLLABORATORS (Idaho National Laboratory): Daniel Schwen, Michele Fullarton, Pierre-Clément Simon, Chao Jiang, Wen Jiang, Andrea Jokisaari

PUBLICATIONS:

Phillpot, S. R., A. C. Antony, L. Shi, M. L. Fullarton, T. Liang, S. B. Sinnott, Y. Zhang, and B. Biner, "Charge Optimized Many Body (COMB) potentials for simulation of nuclear fuel and clad," *Computational Materials Science* 148 (2018), pp. 231–241.



Projects featured in this report have a total cumulative budget of over

$22 MILLION

PROJECT ID: 16-026

INL Initiative: Advance Nuclear Energy

Computationally Efficient Prediction of Containment Thermal Hydraulics Using Multi-scale Simulation

Conventional high-resolution computational fluid dynamics (CFD) approaches are computationally overwhelming for use in long-transient complex-flow simulation in engineering applications, particularly when sensitivity or uncertainty analyses are required to support risk-informed design and safety analysis of nuclear power plants. The goal of this research was to increase the efficiency of computational methods of modeling thermal-hydraulic phenomena. This research developed a technical basis for a coarse-grained CFD capability that is needed for high-fidelity analysis of containment thermal hydraulics. The researchers found that data-driven approaches have the potential to improve system thermal-hydraulic simulations and that the scale gap from the extrapolation of global physics can be bridged by training and learning from local physics. Techniques explored in this work will be applied in new work recently awarded to INL.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Bob Youngblood

INTERNAL COLLABORATOR (Idaho National Laboratory): Hongbin Zhang

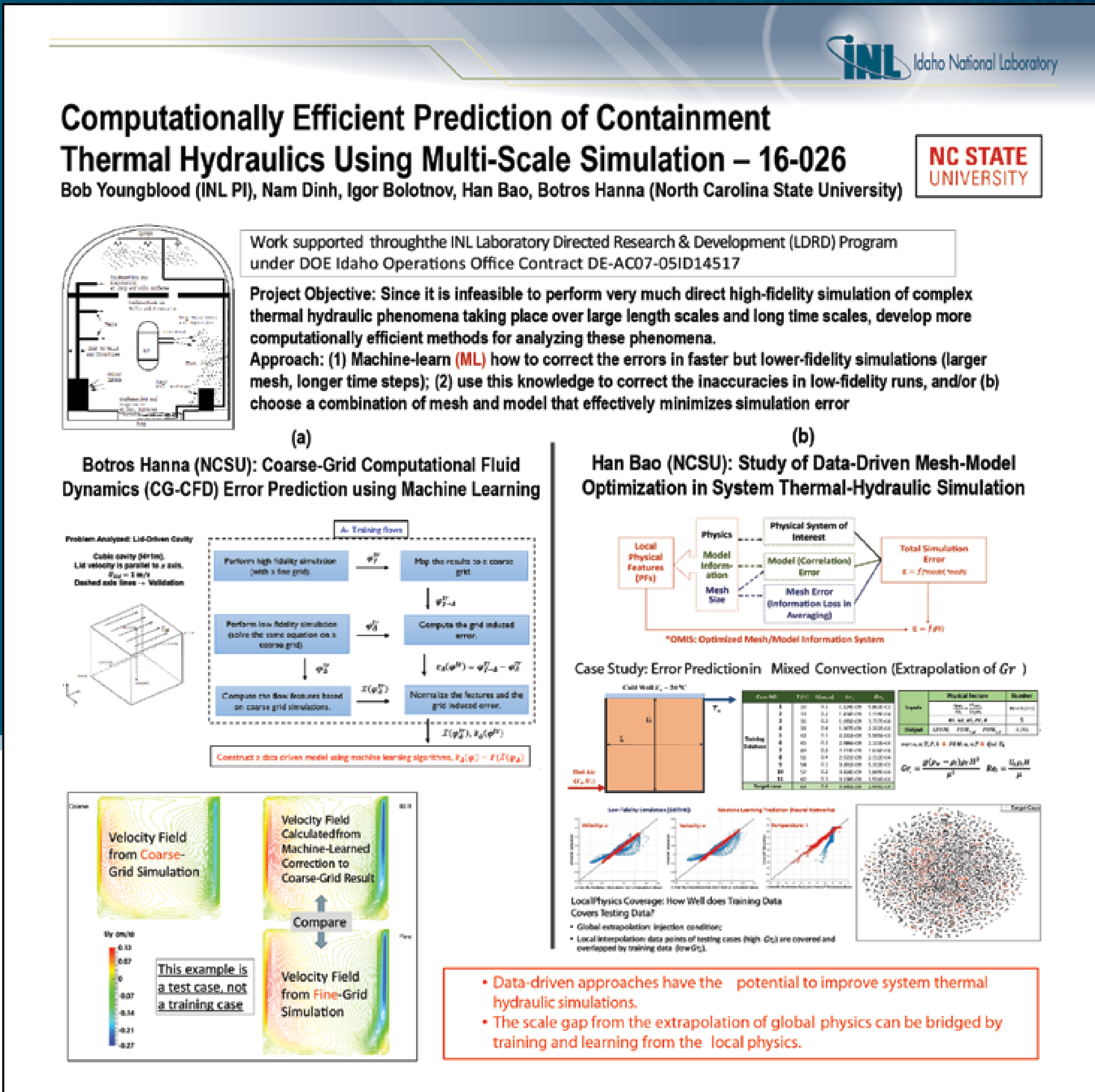
EXTERNAL COLLABORATORS (North Carolina State University): Nam Dinh, Igor Bolotnov, Han Bao, Botros Hanna

DISSERTATION:

Hanna, Botros N., "Coarse-Grid Computational Fluid Dynamic (CG-CFD) Error Prediction using Machine Learning," Ph.D. North Carolina State University, Raleigh, North Carolina, 2018.

PUBLICATIONS:

Bao, H., H. Zhao, H. Zhang, L. Zou, P. Sharpe, and N. Dinh, "Safe reactor depressurization windows for BWR Mark I Station Blackout accident management strategy," *Annals of Nuclear Energy* 114 (2018), pp. 518–529.



Projects featured in this report resulted in

91 conference presentations

PROJECT ID: 16-040

INL Initiative: Advance Nuclear Energy

Integration of Prognostic Techniques and Probabilistic Safety Assessment (PSA) for Online Risk Monitoring

At present in the nuclear industry, risk monitors provide a point-in-time estimate of system risk given a current plant configuration, not taking into account the health information of plant equipment. This research focused on developing an approach to solidify risk monitors to provide time- and condition-dependent risk. This work integrated traditional probabilistic risk assessment models with condition monitoring and prognostic techniques. The main outcome of this work is a novel online risk model that takes into account operational status, aging, and degradation of plant equipment. This research will lead to enhanced operations and risk management at complex facilities and infrastructure. The research outcomes of this project are leveraged by DOE's Light Water Reactor Sustainability Program to perform research on a risk-informed maintenance strategy in collaboration with nuclear industry. This has led to direct funding and industry collaboration. This work has also contributed to a proposal submission under the DOE -issued funding opportunity announcement with industry. In addition, this research has led to several peer-reviewed conference articles and journal articles.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Vivek Agarwal

INTERNAL COLLABORATORS (Idaho National Laboratory): Vaibhav Yadav, Andrei Gribok, Curtis Smith

16-040: Integration of Prognostic Techniques & Probabilistic Safety Assessment (PSA) for Online Risk Monitoring

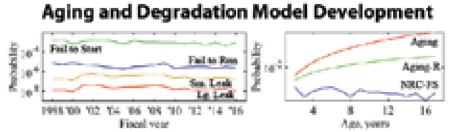
Vivek Agarwal, Vaibhav Yadav, Andrei V. Gribok, and Curtis L. Smith

Research Innovation Achieved

Developed a novel **online risk model** with **both** aging and degradation of plant assets into traditional PSA

- Markov chain and hazard rate-based models to account for component aging and degradation
- Correlation analysis over 15 dimensions was performed. → Vibration and sound amplitude were identified as strongest indicators
- Machine learning to identify change from healthy to degraded state
- Auto-regression moving average model validated to predict motor performance
  - Prognosis was used to update motor failure rate. motor to identify degradation
- Integrated the risk models into traditional PSA framework to obtain probabilities

Aging and Degradation Model Development



NRC industry average does not account for aging

Effect of aging on probability using Markov Chain

Hazard Rate

Probability of a component to survive the next interval $\Delta\tau$ given it has survived τ time intervals

$$\lambda(\tau) = \lim_{\Delta(} \frac{Pr(\tau < t \leq \tau + \Delta\tau | t > \tau)}{\Delta\tau}$$

Exponential Failure Rate Model

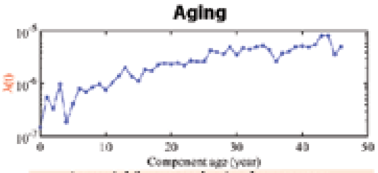
$$\lambda(z) = \lambda_2 exp(\beta z)$$

- z is the measured component condition parameter (vibration, sound, etc.)
- λ_2 is the baseline failure rate or failure rate of healthy component
- β is the unknown coefficient estimated from performance data

Detection of Degradation Onset

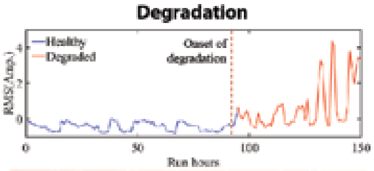
- Machine learning classification (e.g., Support vector machines), and clustering (e.g., k-mean) used to detect onset of degradation

Aging



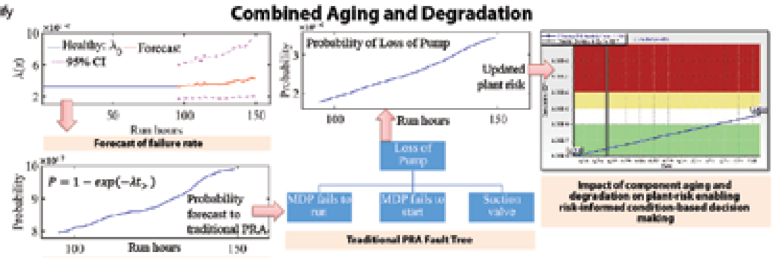
Increase in failure rate as a function of component age

Degradation



Identify onset of degradation to apply prognostic models

Combined Aging and Degradation



Forecast of failure rate

Forecast of probability of failure for degraded component

Traditional PRA Fault Tree

Impact of component aging and degradation on plant-risk enabling risk-informed condition-based decision making

Major Accomplishments

Pipeline

- Hired a post doctoral researcher that led to full time hire
- One summer intern was hired

Publications and Presentations

- **Journal Articles**: 1 submitted and 2 under preparation
- 7 peer-reviewed **conference proceedings**

Impact

This research will lead to enhanced operations and risk management at complex facilities and infrastructure.

Harvest Strategy

- The research will be leveraged by U.S. DOE Light Water Reactor Sustainability Program to develop Integrated Risk-Informed Condition-Based Maintenance Capability with a nuclear utility and a nuclear vendor **(Funding: $5M for 2 years)**

Acknowledgements

- Work supported through the INL Laboratory Directed Research & Development Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517
- ATR Staff: Mr. Robert Fossum & Mr. Bentley Harwood
- The University of Tennessee, Knoxville for the motor degradation data
- Intern: Dr. Payel Chatterjee

Laboratory Directed Research and Development: 2018 Poster Presentation

PROJECT ID: 16-046

INL Initiative: Advance Nuclear Energy

Development of a Synergistic Approach to Study Irradiated Materials Using Coupled Experiments and Simulation

Understanding and predicting the effects of irradiation damage on material properties is possible only when state-of-the-art experimental characterization methods are used in conjunction with advanced mesoscale modeling and simulation. Facilities and testing capabilities exist for microstructural and thermal-properties characterization of irradiated materials, and the Multiphysics Object Oriented Simulation Environment (MOOSE)/MARMOT phase-field modeling code is available for predicting microstructural evolution and its impact on properties in fuel and cladding materials. This project utilized and integrated both experimental and modeling and simulation capabilities to demonstrate an ability to predict thermal conductivity of a metallic fuel system U-Pu-Zr) given its microstructure and binary alloy properties. This model will be added to the large-scale modeling tools for prediction of metallic fuel performance in core that will allow fuel designers to shorten the nuclear fuel-development cycle. Key results included observation of microstructure with electron microscopes. Crystal structure of individual metallic phases was determined with selected-area electron-diffraction patterns. Phase-transition temperatures and energies, as well as thermal conductivity, were measured as a function of annealing and temperature. Direct funding has been secured for this work for Fiscal Year-2019 from the DOE Office of Nuclear Energy to continue measurement of microstructural and thermal properties as a function of low-level irradiation in Transient Reactor Test Facility.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Cynthia Adkins

INTERNAL COLLABORATORS (Idaho National Laboratory and University of Florida): Assel Aitkaliyeva

INTERNAL COLLABORATORS (Idaho National Laboratory): Daniel Wachs

EXTERNAL COLLABORATORS (Pennsylvania State University): Michael Tonks, Jacob Hirschhorn

PUBLICATIONS:

Hirschhorn, J., M. Tonks , A. Aitkaliyeva, and C. Adkins, "Development and Verification of a Phase Field Model for the Equilibrium Thermodynamics of U-Pu-Zr," *Annals of Nuclear Energy* 124 (2019), pp. 490-502.

Award Winner: Second Place in INL Poster Competition

Idaho National Laboratory

Advancing Nuclear Energy

Development of a Synergistic Approach to Study Irradiated Materials Using Coupled Experiments and Simulation

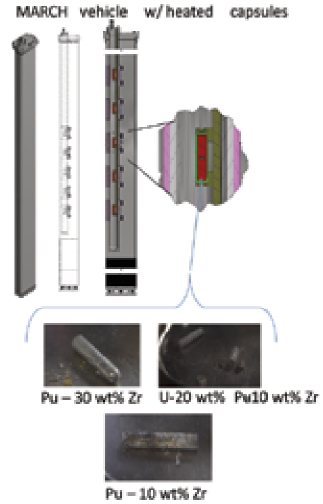
Assel Aitkaliyeva[1,2], Cynthia Adkins[1], Daniel Wachs[1], Michael Tonks[2], Jacob Hirschhorn[2]
[1]Idaho National Laboratory, [2]University of Florida

Objective

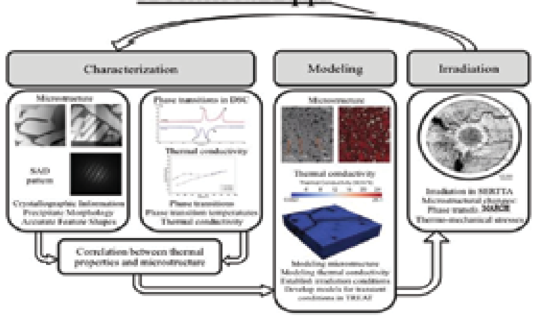
1) develop experimental procedures to obtain the specific pre-and post-irradiation characterization data required for validation and uncertainty quantification of MARMOT models
2) understand the evolution of microstructure under transient irradiation conditions and its impact on properties for use with TREAT.
3) demonstratthe value of a coupled experimental and simulation approach on understanding critical thermal properties in a material of broad interest (the U-Pu-Zrsystem)

Technical Challenges

- New irradiation hardware design was needed to enable irradiation in TREAT – MARCH vehicle
- Leverages TREAT's ease-of-access to measure specimen temperature during irradiation
- TREAT irradiation is scheduled for November 2018

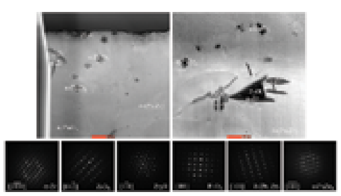


Technical Approach

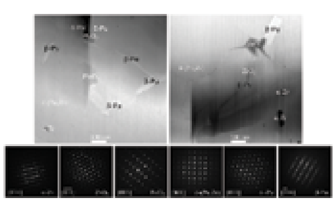


Characterization Results

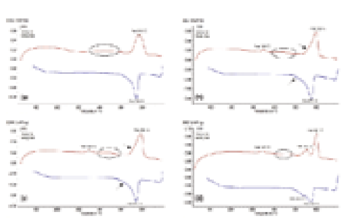
- Microstructure was observed with SEM, TEM and crystal structure determined with SAED patterns (as-cast vs. anneal at TREAT temperature)
- Phase transition temperatures and energies were measured
- Thermal conductivity was measured



Representative phases observed in the as-cast Pu-10Zr specimen. Scale bar denotes 500 nm.



Representative phases observed in the annealed Pu-10Zr specimen. Scale bar denotes 500 nm.



(a) 1st thermal cycle of as-cast material (b) 2nd thermal cycle of as-cast material (c) 3rd thermal cycle of as-cast material (d) 1st thermal cycle of annealed material

DSC signal vs. Temperature (°C) for Pu-10Zr upon heating and cooling

Modeling Results

- Uses measured and published single phase transition temps to predict microstructure evolution with phase-field model

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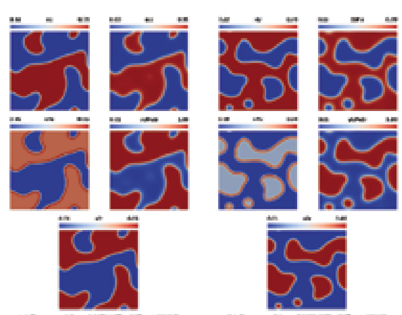


Publications

- Development and Verification of a Phase Field Model for the EquilibriumThermodynamics of U-Pu-Zr, Hirschhorn, Tonks, Aitkaliyeva, Adkins – in review
- The evolution of the microstructure and thermal properties of Pu-10Zr fuels with temperature, Aitkaliyeva, Adkins, Hirschhorn, McKinney, Tonks – in draft
- Thermal Conductivity of Pu-Zr alloys, Adkins, Aitkaliyeva, Hirschhorn, Tonks – in draft
- 9 + presentations in conference proceedings

Future Funding

Irradiation testing of the MARCH capsules in TREAT and the associated PIE characterization will be funded by the NTRD program in FY 2019 sponsored by DOE-NE

Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

Idaho National Laboratory

PROJECT ID: 16-055

INL Initiative: Advance Nuclear Energy

Capability Extension for Multiscale, Multi-application Development Within the Multiphysics Object-oriented Simulation Environment

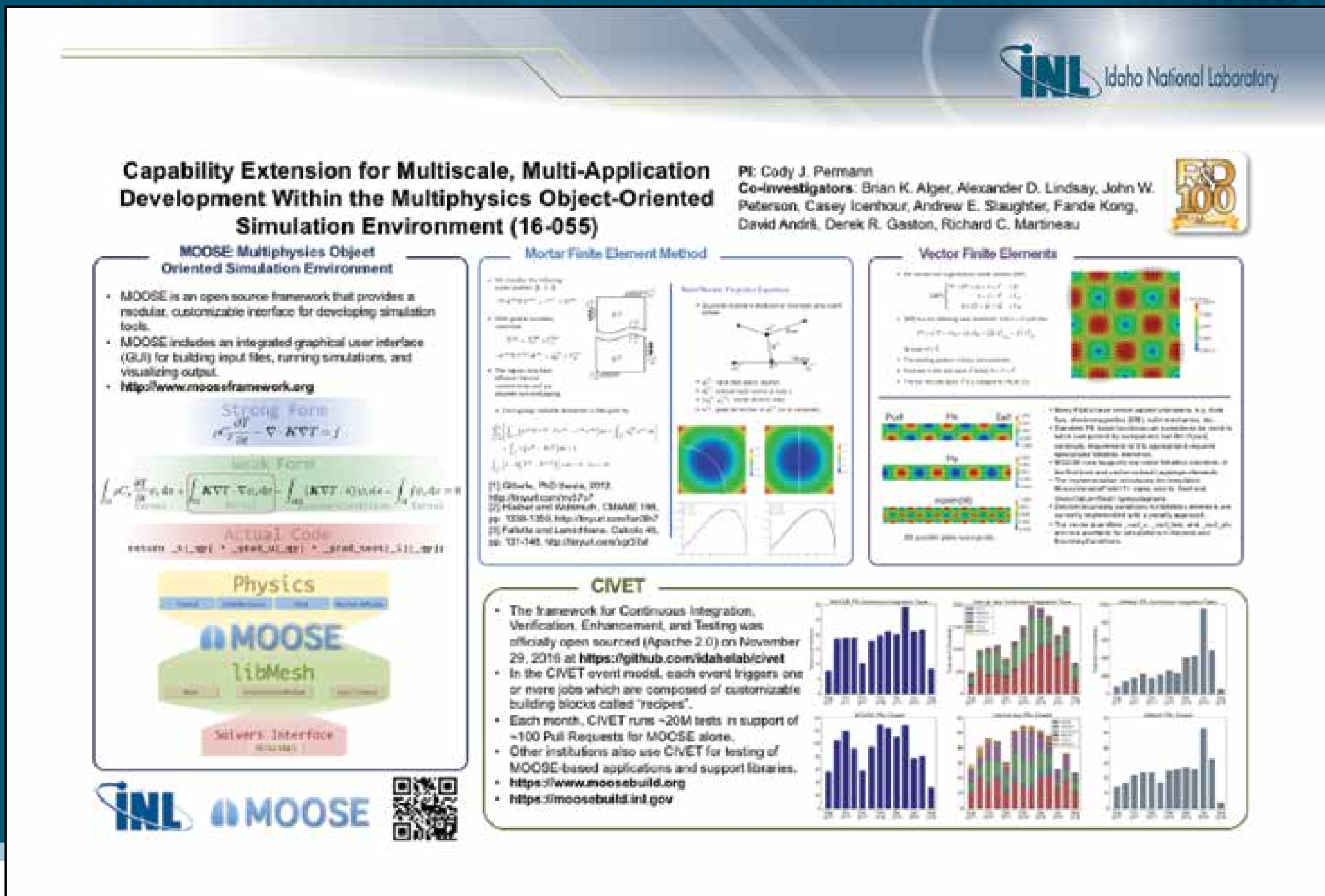
With unique new capabilities added to the framework through this Laboratory Directed Research and Development project, Multiphysics Object Oriented Simulation Environment (MOOSE) remains an attractive platform for performing cutting-edge research on a wide variety of application areas. Several new customers with interests in advanced manufacturing processes, new fuels performance studies, and new subsurface research, have begun evaluating the framework as this research has concluded. These customers will continue to support the ongoing efforts begun by this research as newer capabilities such as the expansion of MOOSE's automatic differentiation, vector kernels, and advanced parallel-distribution research are performed. MOOSE is likely to remain a key asset to the laboratory for the foreseeable future.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Cody Permann

INTERNAL COLLABORATORS (Idaho National Laboratory): Brian Alger, Alexander Lindsay, John Peterson, Casey Icenhour, Andrew Slaughter, Fande Kong, David Andrš, Derek Gaston, Richard Martineau

PUBLICATIONS:

Schwen, D., L.K. Aagesena, J.W. Peterson, and M.R. Tonks, "Rapid multiphase-field model development using a modular free energy based approach with automatic differentiation in MOOSE/MARMOT," *Computational Materials Science* 132 (2017), pp. 36–45.



The **33** projects featured in this report resulted in

10 first filings

14 invention disclosure report

1 license executed

PROJECT ID: 16-058

INL Initiative: Advance Nuclear Energy

Predicting Radiation-induced Microstructural Change via Implementation and Validation of Multiscale Cluster Dynamics in MOOSE

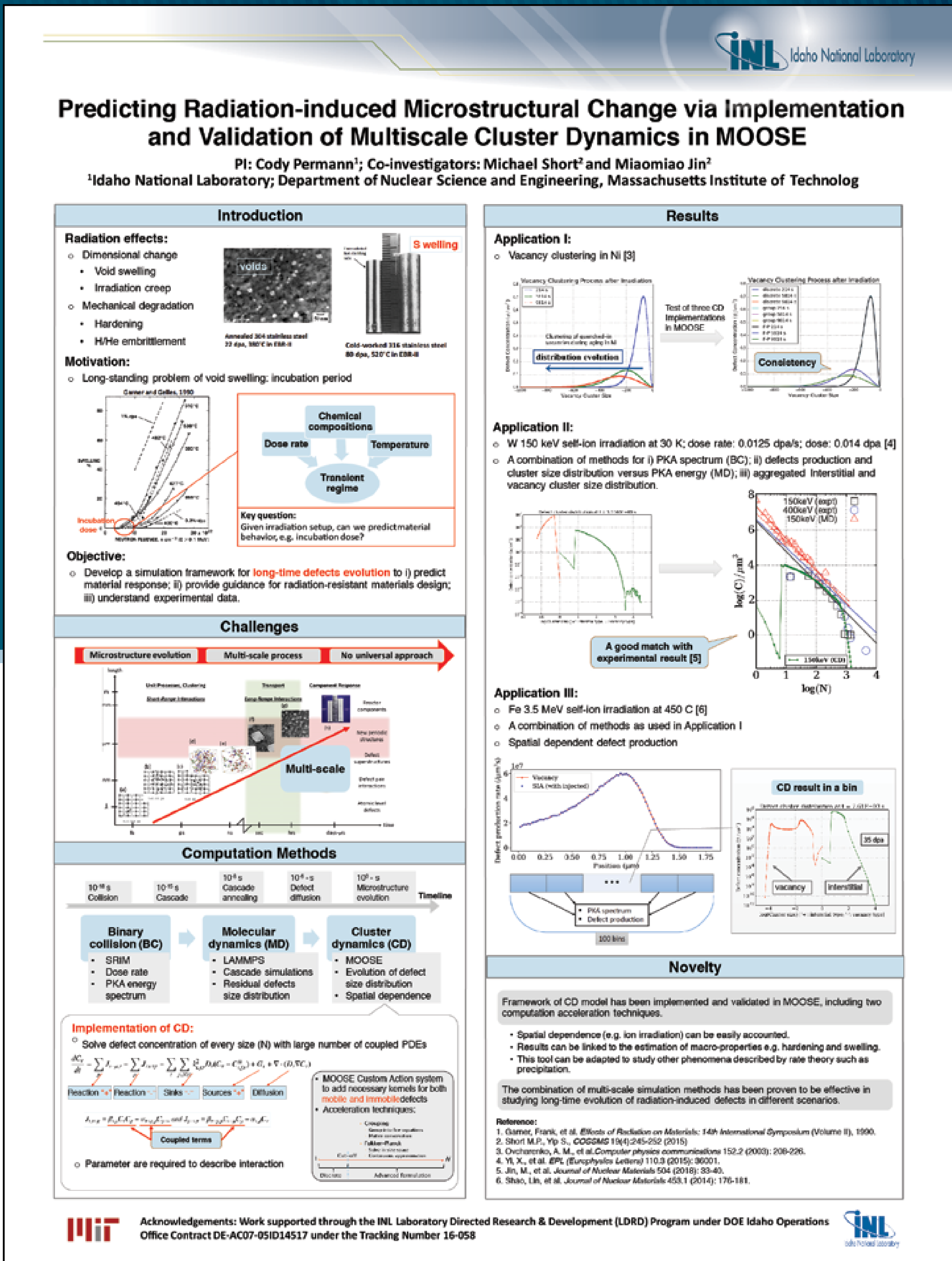
The new cluster-dynamics capability implemented within the Multiphysics Object Oriented Simulation Environment (MOOSE) framework allows for a higher-fidelity scale, bridging effort between atomistic and mesoscale simulations. This ability to run MOOSE-native simulations at scales below the mesoscale will enable the development of even better empirical models for use in the mesoscale and higher-length scale simulations. These new mechanisms can be used to better capture the effects of radiation damage on materials and the physical mechanisms behind those damage models. This will result in better predictive behavior with higher confidence than what is commonly used today.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Cody Permann

EXTERNAL COLLABORATORS (Massachusetts Institute of Technology): Michael Short, Miaomiao Jin

PUBLICATIONS:

Jin, M., C. Permann, and M. P. Short, "Breaking the power law: Multiscale simulations of self-ion irradiated tungsten," *Journal of Nuclear Materials* 504 (June 2018), pp. 33–40.


Idaho National Laboratory
Predicting Radiation-induced Microstructural Change via Implementation and Validation of Multiscale Cluster Dynamics in MOOSE
PI: Cody Permann[1]; Co-investigators: Michael Short[2] and Miaomiao Jin[2]
[1]Idaho National Laboratory; Department of Nuclear Science and Engineering, Massachusetts Institute of Technolog
Introduction
Radiation effects:
Dimensional change
Void swelling
Irradiation creep
Mechanical degradation
Hardening
H/He embrittlement
voids
Swelling
Annealed 304 stainless steel
Cold-worked 316 stainless steel
Motivation:
Long-standing problem of void swelling: incubation period
Garner and Gelles, 1990
Incubation dose
Chemical compositions
Dose rate
Temperature
Transient regime
Key question:
Given irradiation setup, can we predict material behavior, e.g. incubation dose?
Objective:
Develop a simulation framework for long-time defects evolution to i) predict material response; ii) provide guidance for radiation-resistant materials design; iii) understand experimental data.
Challenges
Microstructure evolution
Multi-scale process
No universal approach
Multi-scale
Computation Methods
10^{-18} s Collision
10^{-15} s Cascade
10^{-8} s Cascade annealing
10^{-6} s Defect diffusion
10^{0} s Microstructure evolution
Timeline
Binary collision (BC)
SRIM
Dose rate
PKA energy spectrum
Molecular dynamics (MD)
LAMMPS
Cascade simulations
Residual defects size distribution
Cluster dynamics (CD)
MOOSE
Evolution of defect size distribution
Spatial dependence
Implementation of CD:
Solve defect concentration of every size (N) with large number of coupled PDEs
Reaction
Reaction
Sinks
Sources
Diffusion
Coupled terms
Parameter are required to describe interaction
MOOSE Custom Action system to add necessary kernels for both mobile and immobile defects
Acceleration techniques:
Results
Application I:
Vacancy clustering in Ni [3]
Vacancy Clustering Process after Irradiation
distribution evolution
Test of three CD implementations in MOOSE
Consistency
Application II:
W 150 keV self-ion irradiation at 30 K; dose rate: 0.0125 dpa/s; dose: 0.014 dpa [4]
A combination of methods for i) PKA spectrum (BC); ii) defects production and cluster size distribution versus PKA energy (MD); iii) aggregated interstitial and vacancy cluster size distribution.
150keV (expt)
400keV (expt)
150keV (MD)
150keV (CD)
log(C) / μm³
log(N)
A good match with experimental result [5]
Application III:
Fe 3.5 MeV self-ion irradiation at 450 C [6]
A combination of methods as used in Application I
Spatial dependent defect production
Vacancy
SIA (with injected)
Defect production rate
Position (μm)
PKA spectrum
Defect production
100 bins
CD result in a bin
35 dpa
vacancy
interstitial
Novelty
Framework of CD model has been implemented and validated in MOOSE, including two computation acceleration techniques.
Spatial dependence (e.g. ion irradiation) can be easily accounted.
Results can be linked to the estimation of macro-properties e.g. hardening and swelling.
This tool can be adapted to study other phenomena described by rate theory such as precipitation.
The combination of multi-scale simulation methods has been proven to be effective in studying long-time evolution of radiation-induced defects in different scenarios.
Reference:
1. Garner, Frank, et al. Effects of Radiation on Materials: 14th International Symposium (Volume II), 1990.
2. Short M.P., Yip S., COSSMS 19(4):245-252 (2015)
3. Ovcharenko, A. M., et al. Computer physics communications 152.2 (2003): 208-226.
4. Yi, X., et al. EPL (Europhysics Letters) 110.3 (2015): 36001.
5. Jin, M., et al. Journal of Nuclear Materials 504 (2018): 33-40.
6. Shao, Lin, et al. Journal of Nuclear Materials 453.1 (2014): 176-181.
MIT
Acknowledgements: Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517 under the Tracking Number 16-058
INL Idaho National Laboratory

PROJECT ID: 16-070

INL Initiative: Advance Nuclear Energy

Characterization of Neutron Beamlines at the Neutron Radiography Reactor

The Neutron Radiography Reactor, a 250 kW research reactor located at INL, has two neutron beams designed specifically for neutron radiography. However, information about these neutron beams is limited. This project generated detailed information on the beams, including beam flux, spatial distribution, energy spectrum, divergence, effective collimation ratio, and gamma content. Characteristics of both the east and north beams were measured, and the same measurement techniques were applied at the neutron beam at the Transient Reactor Test Facility. The information gained from these characterization efforts was immediately employed in ongoing efforts to validate radiation-transport models of the beams, to plan experiments and beamline upgrades, and to develop advanced digital neutron-imaging capabilities.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Aaron Craft

INTERNAL COLLABORATOR (Idaho National Laboratory): Glen Papaioannou

EXTERNAL COLLABORATORS (Idaho State University): Sam Giegel, Chad Pope, George Imel

STANDARDS:

This project inspired potential new method for measuring effective length-to-diameter ratio (L/D) that is simpler than the existing ASTM International standard method. INL researchers are working with the ASTM committee to develop this new standard.

IDAHO NATIONAL LABORATORY

ADVANCING NUCLEAR ENERGY

CHARACTERIZATION OF NEUTRON BEAMLINES AT THE NEUTRON RADIOGRAPHY REACTOR

Principal Investigator: Dr. Aaron Craft (INL) Co-Investigators: Sam Giegel (ISU), Dr. Chad Pope (ISU), Glen Papaioannou (INL)

PROJECT OBJECTIVES

- Characterize the neutron beams at the Neutron Radiography Reactor (NRAD) to provide detailed information about these beams to researchers and prospective users.
- Measure the neutron flux, spatial distribution, energy spectrum, and other beam metrics.
- Develop a suite of measurements and methods for future beam characterization efforts at NRAD and TREAT.

IMPORTANCE & BENEFIT

- Detailed information about the NRAD's neutron beams was not available before this project, but is essential to increase the scientific output of one of INL's nuclear reactor facilities.
- Reactor modifications can change the beam characteristics, and this project provides a suite of measurements and pathway for future characterization efforts.
- The detailed beam characteristics provided by this project have already proven beneficial for:
  - Scientific users planning experiments using the neutron beams.
  - Data for verification and validation of radiation transport models of the neutron beams and the NRAD reactor.
  - Calculation of radiation dose rates and expected activation of materials in and near the neutron beams.
  - Inform development of advanced digital neutron imaging capabilities.
  - Inform future modifications to the neutron beams to improve their performance and versatility, and to better accommodate scientific users.
- This project serves as the M.S. thesis project for an Idaho State University graduate student.

METHODS & APPROACH

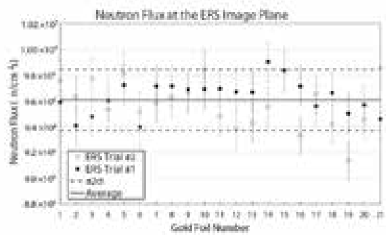
- Neutron flux was measured using foil activation methods.
- Beam uniformity was measured with a neutron radiograph of the open beam.
- Energy spectrum was determined through activation of foils of various materials and subsequent modeling to unfold the energy spectrum that best fits the measured activities.
- These measurements are made for each neutron beam after changes to the reactor that could affect a neutron beam.

ACKNOWLEDGEMENTS

Many thanks to ISU Professors Chad Pope and George Imeland INL's Dr. Aaron Craft and Glen Papaioannou for their guidance and mentorship of the lead researcher, Sam Giegel, an ISU M.S. graduate student at ISU. Additionally, the staff at the NRAD reactor made this work possible through their active involvement taking these measurements.
Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517. LDRD Project ID# 16-070

NEUTRON BEAM FLUX

- Neutron flux was measured by activating an array of 21 gold foils, measuring the resulting activities, then calculating the neutron flux from the measured activities and the average thermal neutron absorption cross-section of gold.



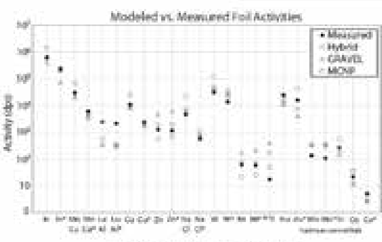
- The foil activation measurements were repeated with an array of 21 cadmium-covered gold foils to measure the cadmium ratio, which is the ratio of the activities of a bare gold and a cadmium-covered gold foils. Cadmium ratio gives an indication of the neutron energy spectrum.

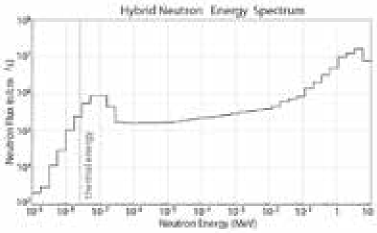
Cadmium Ratio = 2.05 (2 σ=2.9%)

- This cadmium ratio is very low compared to the majority of neutron beams, and indicates that most neutrons in the beam have higher energy than thermal (>0.0253 eV).
- Variation of beam uniformity over the 18 cm wide by 43 cm tall beam area is <3%.

Avg. Neutron Flux ($\phi_{thermal}$) = $9.61 \times 10^{6} \pm 1.47 \times 10^{5}$ n/cm²s

NEUTRON ENERGY SPECTRUM





- The neutron energy spectrum of NRAD's neutron beams had not been measured prior to this project.
- A set of 24 foils of various materials, 13 bare and 11 cadmium-covered, were exposed in the neutron beam and their resulting activities measured.
- The measured activities are then input into UMG (unfolding with MAXED and GRAVEL) software package that calculates the response function of each foil and an initial estimated energy spectrum from MCNP to unfold the neutron energy spectrum.
- Three energy spectra were produced:
  1. MCNP6 model of NRAD and the beamline.
  2. Unfolded spectrum from UMG's GRAVEL program.
  3. Hybrid of both the MCNP and GRAVEL spectra that accounts for anomalies in the GRAVEL calculation's epithermal region.
- Each of these energy spectra were input into an MCNP6 model of the neutron beam to calculate the activity of each foil, and the resulting activities are compared to measured activities in the figure to the top-left.
- The three energy spectra all produce calculated activities that closely match measured activities. The best energy spectrum is the Hybrid because it most closely matches the experimentally measured activities.

PROJECT OUTPUTS

The neutron beams have been characterized and the information garnered has already proven useful.

Talent Pipeline :

The M.S. graduate student, Sam Giegel, has completed his degree and is now employed full time at INL working at TREAT.

Publications :

- S.H. Giegel, C.L. Pope, and A.E. Craft. Characterization of the neutron energy spectrum in a radial neutron beam from a TRIGA reactor. Prepared for submission to J. Applied Physics.
- S.H. Giegel, G.C. Papaioannou, C.L. Pope, and A.E. Craft. Neutron beam characterization at the Neutron Radiography Reactor at Idaho National Laboratory. Prepared for J. Nuc. Eng. &Tech.

Standards :

- This project inspired potential new method for measuring effective length-to-diameter ratio (L/D) that is simpler than the existing ASTM standard method. INL researchers are working with the ASTM committee to develop this new standard.

FACILITY IMPACTS

The energy spectrum revealed a large epithermal and fast neutron component in NRAD's neutron beams, which has significant implications leading to facility modifications:

- INL researchers have begun investigating digital neutron imaging using epithermal neutrons, and plan to investigate potential for imaging with fast neutrons. These could open up entirely new areas of scientific research and increase utilization of the neutron beams.
- The materials used for collimation of the beam are meant for thermal neutrons and have little effect on higher-energy neutrons. Efforts to modify the beams will improve collimation of epithermal and fast neutrons and reduce gamma content.
- Beam shielding materials attenuate thermal neutrons, but are not effective for higher-energy neutrons. A new shielding approach would increase available around the beams that could be used for scientific instruments.
- The energy spectrum informed creation of a new Radiological Controls approach to release samples that were activated in a neutron beam, a necessary step towards NRAD's neutron beams becoming a User Facility.

PROJECT ID: 16-071

INL Initiative: Advance Nuclear Energy

Digital Neutron Imaging Systems for Examination of Irradiated Nuclear Fuel

Neutron radiography provides more comprehensive information about the internal condition of irradiated nuclear fuel than any other non-destructive technique. Neutron radiography for highly radioactive objects typically uses an indirect transfer process with film, and digital systems are typically precluded from use because of their sensitivity to gamma rays emitted by the irradiated fuel. The goal of this work was to test advanced digital neutron-imaging systems for examination of irradiated nuclear fuel. Multichannel plate (MCP) detectors have low estimated gamma sensitivity compared to other digital systems, which may allow their use for evaluating highly radioactive objects. A state-of-the-art MCP system from the University of California at Berkeley was tested at INL to evaluate its potential for imaging irradiated nuclear fuel. This project measured the MCP response to gamma radiation from isotopic sources and produced the first real-time digital neutron radiographs ever produced at INL. Additionally, researchers acquired the world's first fully digital neutron radiographs and the first real-time neutron video of used nuclear fuel. This work demonstrated significant promise for use of such an MCP system for in-situ evaluations and time-resolved imaging of used nuclear fuel.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Aaron Craft

INTERNAL COLLABORATORS (Idaho National Laboratory): Glen Papaioannou, Andrew Smolinski

EXTERNAL COLLABORATOR (University of California, Berkeley): Anton Tremsin

PUBLICATIONS:

Craft, A. E., and J. P. Barton, "Applications of neutron radiography for the nuclear power industry," *Physics Procedia* 88 (2017), pp. 73–80.

Tremsin, A. S., A. E. Craft, M. A. M. Bourke, A. T. Smolinski, G. C. Papaioannou, M. A. Ruddell, J. Littell, and J. Tedesco. "Digital neutron and gamma-ray radiography in high radiation environments with an MCP/Timepix detector," *Nuclear Instruments and Methods in Physical Research Section A* 902 (2018), pp. 110–116.

Idaho National Laboratory

IDAHO NATIONAL LABORATORY

ADVANCING NUCLEAR ENERGY

DIGITAL NEUTRON IMAGING SYSTEMS FOR EXAMINATION OF IRRADIATED NUCLEAR FUEL

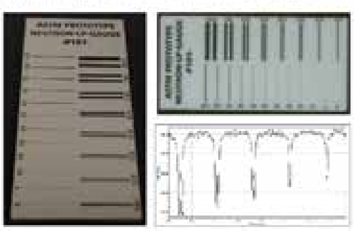
Principal Investigator: Dr. Aaron Craft (INL) Co-Investigators: Dr. Anton Tremsin (UC-Berkeley), Glen Papaioannou (INL), Andrew Smolinski (INL)

PROJECT OVERVIEW

- Goal: Evaluate an advanced micro-channel plate (MCP) detector system with a Timepixreadout developed at UC-Berkeley for its ability to image highly radioactive objects.
- Problem: Radiation emitted from fuel precludes use of most digital imaging technologies, or so was the common wisdom before this project. The current state-of-the-art for neutron imaging of irradiated fuel is still the transfer method with a conversion foil and either film or phosphor image plates.
- Three Main Activities:
  1. Install the MCP system at the Neutron Radiography Reactor (NRAD) North Radiography Station (NRS) to test its ability to produce neutron radiographs with a neutron beam containing high levels of gamma radiation.
  2. Test the MCP's response to gamma-rays using calibrated isotopic gamma sources at INL's Health Physics Instrumentation Laboratory (HPIL).
  3. Based on the success in the previous tests, install the MCP in NRAD's East Radiography Station (ERS) to test its ability to image irradiated nuclear fuel.
- Major accomplishments:
  - Tested MCP detector response to gamma radiation from isotopic sources.
  - Acquired the first real-time digital neutron radiographs ever produced at INL.
  - Acquired the world's first neutron radiographs of used nuclear fuel using a real-time digital imaging system.
  - Leading efforts for new ASTM standards.

NEW STANDARDS FOR DIGITAL NEUTRON IMAGING

- Standards are necessary for quality-controlled applications, such as evaluating nuclear fuels, but there are currently no ASTM standards that technically apply to digital neutron imaging.
- INL researchers are leading development of a new ASTM standard applicable to any neutron imaging system, including digital neutron imaging systems.
- The proposed line-pair gauge uses the same approach as the duplex wire gauge in an existing ASTM standard (E2002).



A picture of the prototype gauge (left), a neutron radiograph of the gauge (top right) and an example line profile (bottom right) showing the contrast between lines for a series line pairs.

- The gauge includes line-pairs spanning 1.0 mm to 5 μm.
- The first set of round robin trials are complete, which included universities, national laboratories, and industrial partners. Based on the lessons learned in the initial round robin, the gauge will be modified for a second round robin.

ACKNOWLEDGEMENTS

The staff at the NRAD reactor made this work possible through their active involvement in planning and taking these measurements.

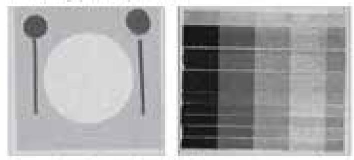
Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517. LDRD Project ID# 16-071

Idaho National Laboratory

INITIAL FEASIBILITY TESTING

- Researchers at INL and UC-Berkeley tested the response of a state-of-the-art MCP system using isotopic gamma sources and in the NRS to determine the detector response.

Schematics of an ASTM beam purity indicator (upper left) and a sensitivity indicator (upper right) and their corresponding digital neutron radiographs acquired with the MCP system (below). These are the first fully-digital neutron radiographs ever acquired at INL.

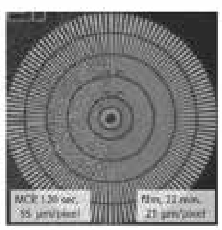


- This was the first time that this MCP system was operated in a radial neutron beam with direct line-of-sight to the reactor core, which causes high gamma content in the neutron beam.
- Measured gamma dose rate in the north beamline ~17.5 m from the core was 812 mSv/hr.

NRAD's Jarod Littell (INL, center) and Anton Tremsin (UC-Berkeley, left) align the detector as Mark Bourke (LANL, right) observes.

Aaron Craft (INL, left) and Anton Tremsin (UC-Berkeley, right) in front of the MCP detector system at the NRS at INL.

- MCP's have lower gamma sensitivity than some other digital systems, so imaging fuel is a question of signal-to-noise ratio.
- Tests in the NRS produced comparable spatial resolution to current film methods, as shown in the radiographs of a test pattern to the right.



IMAGING IRRADIATED FUEL

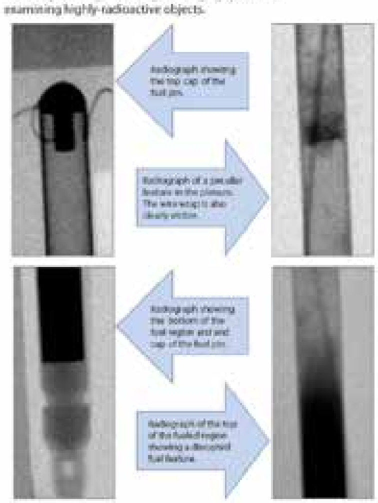
- The MCP system was installed in NRAD's East Radiography Station at the Hot Fuel Examination Facility.

NRAD's Mike Ruddell and Glen Papaioannou setting up a beam collimator.

Dr. Anton Tremsin and Mike Ruddell installing the MCP detector in the East Radiography Station.

Dr. Anton Tremsin and NRAD's Glen Papaioannou evaluating neutron images being produced in real-time.

- The neutron radiographs acquired of an EBR-II X-501 pin exhibit relatively good image quality and demonstrate the feasibility of using such a digital imaging system for examining highly-radioactive objects.



- The top end cap of the fuel pin provided the highest measured gamma dose rate at 5.5 Sv/hr.
- Real-time neutron imaging of the fuel pin was acquired at 20 fps as the fuel was moved vertically in front of the detector.
  - First real-time neutron radiography at INL.
  - First real-time radiography of irradiated fuel worldwide.
- Real-time neutron imaging of the fuel pin was acquired at 20 fps as the fuel was moved vertically in front of the detector.

PROJECT OUTPUTS

Publications:

- A.S. Tremsin, A.E. Craft, M.A.M. Bourke, A.T. Smolinski, G.C. Papaioannou, M.A. Ruddell, J. Littell, and J. Tedesco.Digital neutron and gamma-ray radiography in high radiation environments with an MCP/Timepixdetector. Nuclear Inst. and Methods in Physics Research, A 902 (2018) 110–116.
- A.S. Tremsin, A.E. Craft, G.C. Papaioannou, and A.T. Smolinski, Non-destructive examination of irradiated nuclear fuel assemblies by digital neutron radiography. Prepared for submission in 2018.
- A.E. Craft and J.P. Barton. Applications of neutron radiography for the nuclear power industry. Phys. Procedia 88 (2017) 73-80.

Firsts:

- Produced the first fully-digital neutron radiographs at INL.
- Produced the world's first fully-digital neutron radiographs of irradiated nuclear fuel.
- Produced the world's first real-time digital neutron radioscopy (neutron video) of irradiated nuclear fuel.

New Standards:

- INL researchers are working with the ASTM committee to develop a new ASTM standard for measuring spatial resolution of neutron imaging systems, including digital systems. This effort is related to this project's efforts to move towards digital imaging.

Talent Pipeline:

- Nick Boulton recently completed his M.S. in Radiation Health Physics at Oregon State University. He worked as a subcontractor on this project developing a radiation transport model of the neutron beams. He has since been hired at INL full time.
- INL Summer Intern Russell Jarmerwas supported by this project to investigate neutron contrast agents in liquid penetrants for crack enhancement in neutron radiography.

University Collaborations:

- UC-Berkeley–The primary collaboration for this project was with Dr. Anton Tremsinat UC-Berkeley.
- Colorado School of Mines – Other projects are now supporting continued work with Russell Jarmer, who is now pursuing his PhD, based on the research initially supported by this project.
- Boise State University – This project supported a collaboration with BSU Prof. Elisa Barney-Smith to investigate image processing techniques to improve image quality of digitized neutron radiographs.

Facility Impacts:

- The North Radiography Station returned to service after 23 years of being inoperable to support development of digital neutron imaging systems, including this project.

PROJECT ID: 16-096

INL Initiative: Advance Nuclear Energy

Supporting Operator Performance and Situation Awareness in Highly Automated Nuclear Power Plants

Although issues with high levels of automation are generally well researched, relatively little work has defined how to enable high levels of performance and situational awareness. Further, the majority of research investigating human-automation interaction has been conducted in artificially simplistic laboratory experiments or in contexts such as aviation that do not transfer directly to nuclear power. In this project, researchers investigated the impact of high levels of automation in complex, safety-critical systems and demonstrated ways to enable optimal situational awareness for human operators in those systems. Specifically, this research demonstrated how to design human-automation interaction to support optimal situational awareness, workload, and plant performance in a multi-unit small modular reactor. The project team worked with NuScale Power to investigate the effects of levels of automation on situational awareness, workload, and plant performance in a series of experiments to be conducted in NuScale's control-room simulator. Results support the design of human-automation interaction in the nuclear industry. The results apply to advanced designs and also inform both the use of advanced technologies that may be installed in existing light-water reactors as part of control-room upgrades and the design of systems installed to support grid modernization and hybrid-energy systems.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Katya Le Blanc

INTERNAL COLLABORATORS (Idaho National Laboratory): Zachary Spielman, Rachael Hill, Johanna Oxstrand

EXTERNAL COLLABORATOR (NuScale Power): Ross Snuggerud

Idaho National Laboratory

Supporting operator performance and situation awareness in highly automated nuclear power plants

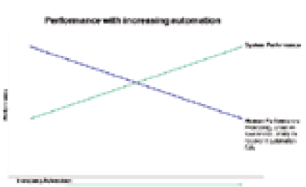
Katya Le Blanc (PI), Ross Snuggerud (NuScale Power), Zachary Spielman, and Rachael Hill

Objective

- Next generation nuclear power plants will need to lower operations and maintenance costs compared to the existing fleet, which means that they will likely have high levels of automation.
- **The objective of this work is to define how to enable human performance under conditions of high levels of automation .**

Technical Challenge

- There is fundamental tradeoff between system performance and human performance with increased automation.
- Scientific research in this area has largely been performed in academic settings with unrealistic tasks, and little research has been conducted in the nuclear power domain.



As automation increases, system performance tends to increase, but human performance shows the opposite trend. The goal of this work is to design a system that simultaneously yields high human performance and high system performance while using high levels of automation.

Approach

Develop design concepts for an automation interface that appropriately engages the human operator while maintaining system performance.

Scientifically test the impact to performance compared to alternative design approaches. The team implemented designs in the NuScale control room simulator and ran 18 operators through controlled scenarios. We measured situation awareness (SA) using combination of objective and subjective measures. We also measured workload, usability, and system performance.

Novelty

- Existing approaches have not yet established how to design highly automated systems that support human performance and situation awareness.
- This research is the first of its kind. to be conducted in a high fidelity simulator with trained operators, and realistic scenarios.

The automation in this interface provides suggested actions (which support system performance) and the supporting information for the operator to approve actions (which supports human engagement in the decision making) and finally provides a validation of plant impact of actions to be taken by human automation team.

Results

Results showed that providing operator with information needed to validate automated suggestions improved situation awareness, reduced workload and increased usability. This was true even for the interface with "too much" information.

Impacts and Outcomes

- Supported licensing process for advanced reactors by developing criteria and methodologies for measuring human performance.
- Developed human automation interaction concepts that were implemented in the NuScale control room and will inform effective human-system interaction for advanced reactors.
- Publications
  - 2 peer reviewed conference papers (1 published, 2 under review).
  - 2 journal articles in preparation.
- Supported 3 interns.
- Developed proposal with ISU nuclear engineering to develop effective human. performance metrics in complex high consequence environments.

8 Post Doctoral Researchers were funded through projects featured in this report

PROJECT ID: 17A1-105

INL Initiative: Advance Nuclear Energy

Safety Margin Evaluation for Experiment Irradiation in Advanced Test Reactor

The current safety basis for the Advanced Test Reactor (ATR) ensures that plant protection criteria are maintained for all Condition 2 events by establishing a departure from nucleate boiling ratio (DNBR) limit. The basis used to establish this limit is not well defined, but may be traced to research-reactor licensing established on overly conservative thermal-hydraulic criteria. This limitation may not be applicable to reactor experiments because the quantity of fissionable material in experiments is much less than that in driver fuel. The limit may prevent or restrict future experimental testing in the ATR. This project evaluated the DNBR limit using various departure from nucleate boiling correlations and considered a statistical approach to evaluate the safety margin in experiments inserted into ATR. The project involved evaluating thermal-hydraulic models of previous experiments that have challenged the safety limits in ATR, examining the safety margin in those experiments, and determining whether the safety margin can be reduced without challenging plant-protection criteria. Based on the safety margin discovered as part of this research, additional funding from ATR programs is continuing this work with the intent of implementing a statistical approach to ensure appropriate margin exists. Additionally, the recovery of safety margin allows for expanding experiment capabilities at ATR.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Joseph Nielsen

INTERNAL COLLABORATORS (Idaho National Laboratory): Paul Murray, Ryan Marlow

EXTERNAL COLLABORATORS (Massachusetts Institute of Technology): Lin-wen Hu, Kaichao Sun, Akshay Dave, Yu-Jou Wang

Idaho National Laboratory

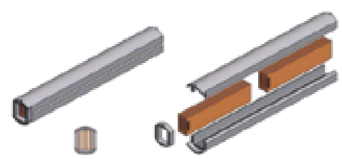
Nuclear Reactor Laboratory

Advancing Nuclear Energy
Safety Margin Evaluation for Experiment Irradiation in Advanced Test Reactor

Idaho National Laboratory
Joseph Nielsen, PhD (PI), Paul Murray, PhD (Co-PI), Ryan Marlow (Co-PI)
Massachusetts Institute of Technology
Lin-wen Hu, PhD (Co-PI), Kaichao Sun, PhD (Co-PI), Akshay Dave, PhD (Post Doc), Yu-Jou Wang (Graduate Student)

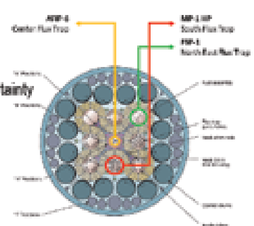
Project Objectives

- Expand the ATR Irradiation Capabilities by developing methodology to quantify uncertainty in thermal-hydraulic analysis for experiments inserted into ATR
- ATR Safety Basis Requires a Departure from Nuclear Boiling Ration (DNBR) and Flow Instability Ratio (FIR) >2.0 for all non-loop experiments or maintain 3σ DNBR and FIR
- ATR Safety Basis limits have prevented or required re-design of experiments to meet Deterministic Limits



Approach

- Evaluate currently various CHF and FIR correlations to estimate safety margin for experiments inserted into ATR.
- Use existing RELAP5 models of previously irradiated and future experiment to evaluate uncertainty in DNBR and FIR using RAVEN and DAKOTA.
- Three experiments with different power distribution cases were considered
  - Case 1 Best estimate power
  - Case 2 Best estimate plus uncertainty
  - Case 3 Conventional factors plus uncertainty



Technical Challenges

- Statistical method currently allowed under safety basis for experiments has never been used due to complexity, schedule and funding
- Need to identify statistical parameters that have significant effect on uncertainty
- Currently used Critical Heat Flux Correlations and Flow Instability Correlations are outdated and does not cover thermal-hydraulic conditions in ATR

Novelty

- Use of the Risk Informed Safety Margin Characterization (RISMC) methodology applied to INL operating facilities
- Methodology can be applied to alleviate ATR operating restrictions (Outer Shim Control Cylinder limits).
- Evaluated to use of Transient CHF model for additiona margin
- Findings can be applied to recapture safety margin in ATR and uprate maximum lobe power

	Power Factors					Hydraulic Factors			
	Core power factor	Plate Power Peaking Factor	Outer shim flux multiplier	Power measurement uncertainty	Fissile material loading factor	Pressure	Mass flow rate	Inlet Subcooling	Flow Area
Experiment MP-1 / FSP-1 / AFIP-6	1.277 / 1.750 / 1.500	1.15 / 1.10 / 1.10	1.09 / N/A / N/A	1.085 / 1.085 / 1.085	1.15 / 1.15 / 1.15	[illegible]	[illegible]	[illegible]	[illegible]
Conventional	Constant	Constant	Constant	Constant	Constant	N/A	N/A	N/A	N/A
Case 1: Best Estimate (BE)	Constant	Constant	Constant	N/A	N/A	Statistical	Statistical	Statistical	Statistical
Case 2: Best Estimate Plus Uncertainty (BEPU)	Constant	Constant	Constant	Statistical [illegible]	Statistical [illegible]	Statistical	Statistical	Statistical	Statistical
Case 3: Conventional Factors Plus Uncertainty (CFPU)	Constant	Constant	Constant	Constant	Constant	Statistical	Statistical	Statistical	Statistical

CHFR		MP-1 Mean	3σ	3σ [%]	μ-3σ	FSP-1 Mean	3σ	3σ [%]	μ-3σ	AFIP-6 Mean	3σ	3σ [%]	μ-3σ
Case 1 BE	LUT 1986	1.57	0.05	3.2%	1.52	1.94	0.07	3.5%	1.87	1.36	0.04	3.1%	1.31
	LUT 2006	2.18	0.11	5.2%	2.07	2.81	0.14	5.0%	2.67	2.27	0.08	3.4%	2.20
	LUT 2006-M	2.44	0.24	9.8%	2.20	3.20	0.29	9.0%	2.91	2.80	0.19	6.8%	2.62
	SRL-A	2.39	0.38	15.9%	2.01	4.04	0.53	13.2%	3.51	3.75	0.48	12.8%	3.28
	SRL-B	1.92	0.26	13.7%	1.66	3.17	0.34	10.7%	2.83	2.88	0.29	10.0%	2.59
	HM	3.30	0.20	5.9%	3.11	4.16	0.21	5.1%	3.94	3.03	0.18	6.0%	2.85
Case 2 BEPU	LUT 1986	1.59	0.48	30.5%	1.10	1.96	0.58	29.6%	1.38	1.37	0.41	29.9%	0.96
	LUT 2006	2.24	0.79	35.3%	1.45	2.83	0.98	34.7%	1.85	2.29	0.71	31.0%	1.58
	LUT 2006-M	2.55	0.92	36.2%	1.63	3.23	1.15	35.5%	2.08	2.82	0.88	31.2%	1.94
	SRL-A	2.55	1.00	39.5%	1.54	4.08	1.54	37.8%	2.54	3.78	1.22	32.3%	2.56
	SRL-B	2.03	0.75	37.3%	1.28	3.20	1.12	34.9%	2.08	2.89	0.86	29.7%	2.03
	HM	3.39	0.92	27.0%	2.47	4.19	1.15	27.5%	3.03	3.05	0.85	27.9%	2.20
Case 3 CFPU	LUT 1986	1.23	0.04	3.2%	1.19	1.51	0.06	3.9%	1.45	1.08	0.11	10.2%	0.97
	LUT 2006	1.64	0.10	6.3%	1.54	2.07	0.13	6.4%	1.94	1.78	0.12	6.7%	1.66
	LUT 2006-M	1.86	0.21	11.2%	1.66	2.37	0.25	10.5%	2.12	2.19	0.29	13.0%	1.91
	SRL-A	1.84	0.33	17.7%	1.51	2.95	0.44	15.0%	2.51	2.92	0.39	13.3%	2.53
	SRL-B	1.49	0.22	15.1%	1.26	2.36	0.30	12.6%	2.06	2.26	0.24	10.7%	2.02
	HM	2.70	0.16	6.0%	2.54	3.30	0.18	5.3%	3.13	2.41	0.15	6.1%	2.26

OFIR RELAP5 / OFIR		MP-1 Mean(μ)	3σ	3σ [%]	μ-3σ	FSP-1 Mean(μ)	3σ	3σ [%]	μ-3σ	AFIP-6 Mean(μ)	3σ	3σ [%]	μ-3σ
Case 1 BE	INL	3.24	0.44	13.7%	2.80	3.13	0.38	12.2%	2.75	8.19	1.19	14.6%	7.00
	SZ	3.08	0.67	21.6%	2.41	5.84	1.08	18.5%	4.76	5.31	0.91	17.2%	4.39
	WF	2.36	0.32	13.6%	2.03	2.61	0.32	12.1%	2.29	5.76	0.84	14.6%	4.92
Case 2 BEPU	INL	3.44	1.04	30.2%	2.40	3.15	0.93	29.6%	2.23	8.23	2.44	29.6%	5.80
	SZ	3.35	1.44	43.1%	1.91	5.91	2.55	43.1%	3.36	5.34	1.88	35.2%	3.46
	WF	2.50	0.75	30.2%	1.74	2.63	0.77	29.4%	1.86	5.79	1.71	29.6%	4.08
Case 3 CFPU	INL	2.73	0.37	13.7%	2.35	2.50	0.31	12.3%	2.19	6.59	0.99	15.0%	5.61
	SZ	2.38	0.56	23.4%	1.83	4.12	0.87	21.1%	3.25	4.08	0.74	18.2%	3.34
	WF	1.98	0.27	13.6%	1.71	2.08	0.26	12.3%	1.82	4.64	0.69	15.0%	3.94

(green) $\mu - 3\sigma > 1.2$
(yellow) $1.0 > \mu - 3\sigma > 1.2$
(red) $\mu - 3\sigma < 1.0$

Findings

Significant increase in margin with a statistical method ($\mu - 3\sigma > 1.2$) compared to the conventional ($CHFR > 2.0$)

Experiment	Method	CHFR Correlations LUT 2006-M	CHFR Correlations SRL-A
MP-1	Conventional	-6.8%	-8.2%
	Case 3 CFPU	37.9%	25.9%
FSP-1	Conventional	18.3%	47.7%
	Case 3 CFPU	76.4%	109.2%
AFIP-6	Conventional	9.7%	46.1%
	Case 3 CFPU	59.0%	111.1%

PROJECT ID: 17P10-003

INL Initiative: Advance Nuclear Energy

Small-scale Mechanical Testing of Irradiated Ferritic Stainless Steels

Development of advanced reactor materials that can withstand nuclear reactor environments is crucial for the license extension of current nuclear reactors and the design of future advanced-reactor concepts. Under irradiation, the formation of defects can significantly degrade the mechanical properties of reactor materials. It is reported in the literature that nano-features, such as nanoparticles and nanograins in nanostructured materials, can trap defects and mitigate the mechanical degradation of materials, while a direct correlation of irradiated microstructure and mechanical properties is still missing. This project established the relationship between microstructure and mechanical properties of irradiated nanostructured ferritic stainless steels by using small-scale mechanical testing techniques. Simultaneous correlation of microstructural development and mechanical-property evolution provides information on how irradiated materials fail under deformation. Our research result demonstrates a new approach of testing radioactive materials and provides scientific insights on the design of microstructure and chemical composition of advanced materials for nuclear reactors. The results of this project were used to acquire direct funding from DOE.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Cheng Sun

INTERNAL COLLABORATORS (Idaho National Laboratory): Mitchell Meyer, Jian Gan

PUBLICATIONS:

Aydogan, E., S.A. Maloy, O. Anderoglu, C. Sun, J.G. Gigax, L. Shao, F.A. Garner, I.E. Anderson, and J.J. Lewandowski, "Effect of tube processing methods on microstructure, mechanical properties and irradiation response of 14YWT nanostructured ferritic alloys," *Acta Materialia* 134 (2017), pp. 116–127.

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Sun, C., L. Malerba M.J. Konstantinovic, F.A. Garner, S. A. Maloy, "Emulating neutron-induced void swelling stainless steels using ion irradiation," Proceedings of 18th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 2017, pp. 669–680.

Weaver, J., C. Sun, Y. Wang, S.R. Kalidindi, R.P. Doerner, N.A. Mara, and S. Pathak, "Quantifying the mechanical effects of He, W and He + W ion irradiation on tungsten with spherical nanoindentation," *Journal of Materials Science* 53.7 (2018), pp. 5296–5316.

Zhang, Z., K. Hattar, Y. Chen, L. Shao, J. Lia, C. Sun, K. Yu, N. Li, M.L. Taheri, H. Wang, J. Wang, and M. Nastasi, "Radiation damage in nanostructured materials," *Progress in Materials Science* 96 (2018), pp. 217–321.

Small-scale mechanical testing of irradiated ferritic stainless steels

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LDRD initiative: Advanced Nuclear Energy (ANE). Tracking number: 17P10-003FP

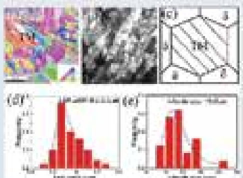
Introduction

- Challenges:
  1. Irradiation damage can significantly degrade the mechanical properties of nuclear fuels and materials thus the safety and reliability of nuclear reactors[1-2].
  2. Significant hazards, cost and time required for post-irradiation examination.
- Objectives:
  1. Enhance the irradiation tolerance of materials by nano-engineering.
  2. Develop a high-throughput mechanical testing capability to shorten the nuclear fuel and material development cycle.

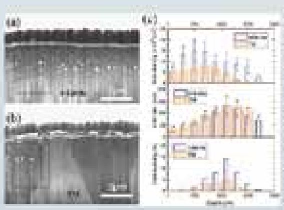
Scientific Approaches

- Methods:
  1. Microstructure characterization (transmission electron microscopy and atom probe tomography)
  2. Small-scale mechanical testing (nanoindentation, micro-pillar compression and micro-tensile test)
  3. Crystal plasticity finite element modeling in MOOSE.
- Novelty:
  1. Measurement of mechanical properties of irradiated materials using small-scale techniques.
  2. Coupling of crystal plasticity finite element models and experiment measurement to understand materials failure mechanism.

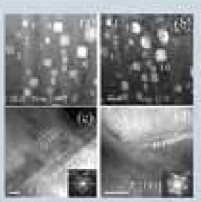
Comparison of void swelling in ferritic/martensitic stainless steels



Tempered martensite (lath structure) and delta ferrite (equiaxed grain structure) coexist in Fe-9Cr alloy.



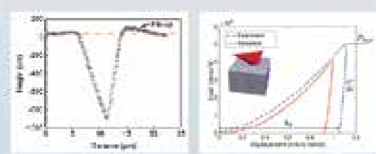
Voids form in both phases under Fe ion irradiation. TM phase exhibits stronger void swelling resistance compared to delta ferrite.



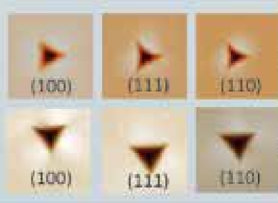
The geometry of the voids in Fe-9Cr under Fe ion irradiation. At zone axis of [001], the side of the void is parallel to {110} plane. At zone axis of [111], the side of the void is parallel to {110} planes.

Nanoindentation-induced pile-ups in Fe-9Cr alloy

Orientation-dependent nanoindnetation tests of Fe-9Cr. A sharp Berkovich indenter was used to probe the material.



An example of nanoindentaion-induced pile-up (left). Load-displacement curve simulated by crystal plasticity constitutive model in MOOSE (right).

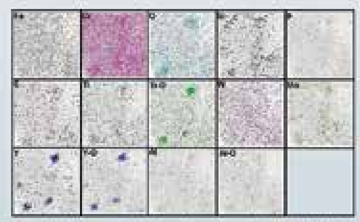


Simulation

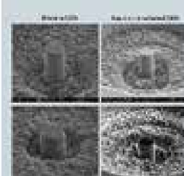
Experiment

Micro-pillar compression test of neutron irradiated 9CrYWT ODS alloy

Typical bcc structured ferrite (grain size ~500nm). Bi-model distribution of nano-clusters: ~50 nm (large) and ~5 nm (small).



Atom probe tomography of neutron irradiated 9CrYWT ODS alloy. Yi-O and Ti-O nano-clusters were observed.



Comparison of load-displacement curve of pristine and neutron irradiated ODS alloy.

Awarded funding

- C. Sun (PI), D. L. Porter, W. Jiang, F. A. Garner, "Understanding swelling-related embrittlement of AISI316 stainless steel irradiated in experimental breeder reactor II", DOE-NE, CINR-NSUF, FY19-21.
- J. Li, M. K. Meyer, C. Sun (Co-PI), "Nanodispersion strengthened metallic composites with enhanced neutron irradiation tolerance", DOE-NE, CINR-NSUF, FY19-21
- C. Sun (PI), Y. Zhang, "Coupling of modeling and experiment to develop predictive models of the mechanical behavior of nuclear fuels and materials", INL/LDRD, FY17-21

Publications

- X. Zhang, K. Hattar, M. L. Taheri, N. Li, Y. Chen, C. Sun, et al., Progress in Materials Science, 96(2018):217-321.
- C. Sun, F. Garner, et al., Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 409 (2017), 323-327.
- C. Sun, L. Malerba, et al., Proceedings of 18th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 2017, pp 669-680.

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1. G. Was, *Fundamentals of Radiation Materials Science, 2017.*
2. K. L. Murty, *Structural materials for Gen-IV nuclear reactors: challenges and opportunities, J. Nucl. Mater., 2008*

Acknowledgement

The work is supported through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517. We also acknowledge the U.S. Department of Energy, Office of Nuclear Energy under DOE Idaho Operation Office Contract DE-AC07-05ID14517 as part of a Nuclear Science User Facility (NSUF) experiment.

PROJECT ID: 18P37-003

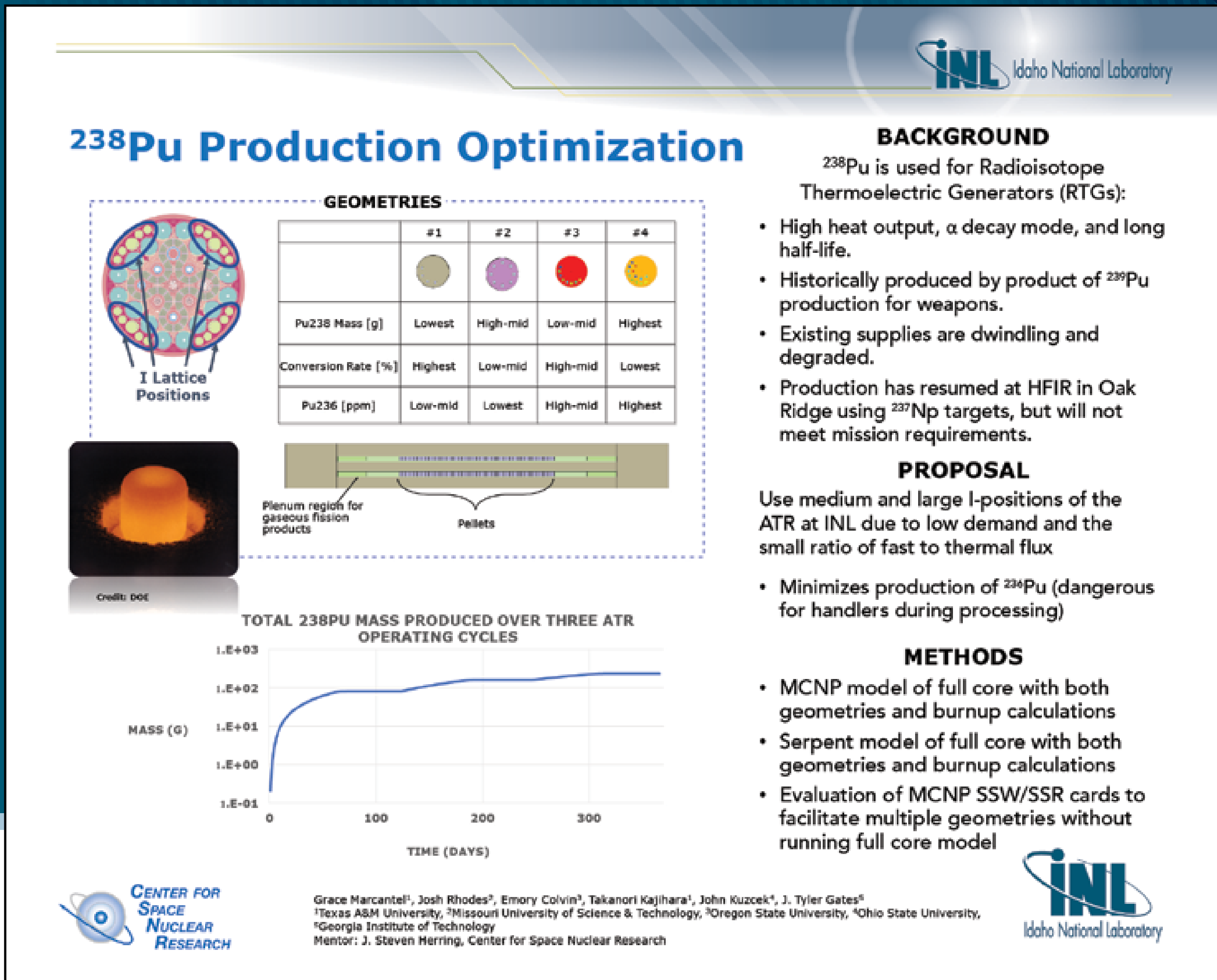
INL Initiative: Advance Nuclear Energy

Plutonium-238 Production Optimization

The creation of isotopes for energy is typically accomplished using either a reactor or an accelerator to bombard a target comprising a stable isotope and to create the desired reactive isotope. There are few nuclear reactors available in the research and development arena in the U.S. that can be utilized in this capacity, and the use of an accelerator frequently does not yield isotopes in usable macroscopic quantities. The production of isotopes that decay in a manner conducive to producing electrical energy from them is of interest in many different areas, such as defense, space, and environmental monitoring applications. The goal of this project was to explore using the ATR as a computational base for isotope production and to quantify the production of isotopes and their enrichment assay. The mere production of isotopes is insufficient to enable their use, and a sound method of encapsulating them in a robust, but affordable manner is required so that their basic function (i.e., providing the energy of radioactive decay) is not hindered. Developing a modeling approach that is based on first principles and can examine the iridium/oxygen/plutonium dioxide system using chemical and thermodynamic tools was part of this work.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Stephen Johnson

INTERNAL COLLABORATOR (Idaho National Laboratory): Brad Kirkwood


Idaho National Laboratory
238Pu Production Optimization
GEOMETRIES
I Lattice Positions
#1 #2 #3 #4
Pu238 Mass [g] Lowest High-mid Low-mid Highest
Conversion Rate [%] Highest Low-mid High-mid Lowest
Pu236 [ppm] Low-mid Lowest High-mid Highest
Plenum region for gaseous fission products
Pellets
Credit: DOE
TOTAL 238PU MASS PRODUCED OVER THREE ATR OPERATING CYCLES
MASS (G)
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
0
100
200
300
TIME (DAYS)
BACKGROUND
238Pu is used for Radioisotope Thermoelectric Generators (RTGs):
• High heat output, α decay mode, and long half-life.
• Historically produced by product of 239Pu production for weapons.
• Existing supplies are dwindling and degraded.
• Production has resumed at HFIR in Oak Ridge using 237Np targets, but will not meet mission requirements.
PROPOSAL
Use medium and large I-positions of the ATR at INL due to low demand and the small ratio of fast to thermal flux
• Minimizes production of 236Pu (dangerous for handlers during processing)
METHODS
• MCNP model of full core with both geometries and burnup calculations
• Serpent model of full core with both geometries and burnup calculations
• Evaluation of MCNP SSW/SSR cards to facilitate multiple geometries without running full core model
Center for Space Nuclear Research
Grace Marcantel1, Josh Rhodes2, Emory Colvin3, Takanori Kajihara1, John Kuzcek4, J. Tyler Gates5
1Texas A&M University, 2Missouri University of Science & Technology, 3Oregon State University, 4Ohio State University, 5Georgia Institute of Technology
Mentor: J. Steven Herring, Center for Space Nuclear Research
Idaho National Laboratory

PROJECT ID: 15-146

INL Initiative: Clean Energy Deployment

Tailoring the Kinetic Function of a Surface through Electronic Effects of Nanoscale Architecture

Catalytic materials enable the energy-efficient manufacture of essential chemicals that are the starting point of most consumer products. These materials are complex, not only in composition and structure, but also with respect to the reaction mechanisms controlled by the surface. The goal of this project was to understand how complex nanoscale architectures control different parts of a reaction mechanism using transient kinetics. Ultimately, this will guide the tailoring of catalytic architectures to orchestrate a desired sequence of steps in a complex industrial reaction mechanism. This research resulted in an increased understanding of these reactions using transient kinetics and atomic-layer deposition. The researchers used a unique INL capability for transient experiments, the Temporal Analysis of Products reactor to better understand water-gas shift chemistry as well as how catalysts can be made more active, energy efficient, and durable. The results of this research have already been used in proposals that resulted in direct funding from the DOE Advanced Manufacturing Office.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Rebecca Fushimi

INTERNAL COLLABORATORS (Idaho National Laboratory): Zongtang Fang, Lucun Wang, Ross Kunz

EXTERNAL COLLABORATORS: Shuai Tan, Dongmei (Katie) Li (University of Wyoming); Denis Constales (Ghent University); Gregory Yablonsky (Washington University)

PUBLICATIONS:

Baroi, C., A. Gaffney, and R. Fushimi, "Process economics and safety considerations for the oxidative dehydrogenation of ethane using the M1 catalyst," *Catalysis Today* 298 (2017), pp. 138–144.

Constales, D., Gregory S. Yablonsky, L. Wang, W. Diao, V.V. Galvita and R. Fushimi, "Precise non-steady-state characterization of solid active materials with no preliminary mechanistic assumptions," *Catalysis Today* 298 (2017), pp. 138–144.

Fushimi, R. and J. Gleaves, "Recent advances in dynamic chemical characterization using Temporal Analysis of Products," *Current Opinion in Chemical Engineering* 21 (2018), pp. 10–21.

Kunz, M. R., E. Redekop, G. Yablonsky, D. Constales, L. Wang, T. Borders, and R. Fushimi, "Pulse Response Analysis Using the Y-Procedure Computational Method," *Chemical Engineering Science* 192 (2018), pp. 46–60.

Lwin, S., W. Diao, C. Baroi, A. Gaffney, and R. Fushimi, "Characterization of MoVTeNbOx Catalysts during Oxidation Reactions Using In Situ/Operando Techniques: A Review," *Catalysts* 7.4 (2017), p. 109.

Morgan, K., N. Maguire, R. Fushimi, J. T. Gleaves, A.G. Goguet, M. P. Harold, E. V. Kondratenko, U. Menon, Y. Schuurman, and G. S. Yablonsky, "Forty Years of Temporal Analysis of Products," *Catalysis Science & Technology* 7 (2017), pp. 2416–2439.

Tan, S., S. Wang, S. Saha, R. Fushimi, and D. Li, "Active Site and Electronic Structure Elucidation of Pt Nanoparticles supported on phase-pure Molybdenum carbide nanotubes," *ACS Applied Materials and Interfaces* 9.11 (2017), pp. 9815–9822.

Wang, L. C., C. M. Friend, R. Fushimi, and R. Madix, "Activation of Dioxygen and Methanol at Active Sites on Silver/Gold Nanoporous Catalysts," *Faraday Discussions* (2016), p. 188.

NUMBER OF INVENTION DISCLOSURE REPORTS: 1

Tailoring the Kinetic Function of a Surface through Electronic Effects of Nanoscale Architecture

Principal Investigator: **Rebecca Fushimi**[1] Project Number 15-146 LDRD Initiative: Clean Energy Deployment

Co Investigators: Zongtang Fang[1], M. Ross Kunz[1], Lucun Wang[1], Shuai Tan[2], Dongmei (Katie)Li[2], Denis Constales[3], Gregory S.Yablonsky[4]

[1] Biological and Chemical Processing Department, Idaho National Laboratory, Idaho Falls, ID 83401
[2] Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071
[3] Department of Mathematical Analysis, Ghent University, Galglann 2, B-9000 Gent, Belgium
[4] Department of Energy, Environment and Chemical Engineering, Washington University in Saint Louis, Saint Louis, MO 63103

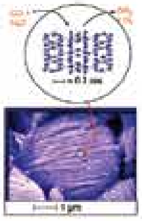
Introduction

❖A catalyst is used to control the selectivity and energy efficiency of a chemical reaction.

❖A catalyst surface is a complex multicomponent, multiphasic structures that is difficult to characterize.

❖A global chemical transformation is orchestrated on a surface by a series of elementary steps that comprise a microkinetic mechanism.

❖Transient experiments can provide greater kinetic detail for understanding reaction networks that take place on complex surfaces.



Project Objective

❖Create new understanding for how nanoscale architectures on a complex catalytic surface control reaction networks using transient kinetics.

Approach

❖**Materials**: Controlled synthesis of nanoscale architectures using atomic layer deposition (ALD).

❖**Experiment**: Temporal Analysis of Products (TAP) pulse response transient kinetic characterization of elementary reaction steps.

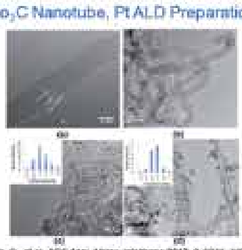
❖**Theory:** Atomistic modeling support to understand kinetic experiments.

Materials

❖Phase-pure Mo_2C nanotubes decorated with Pt domains (2 and 2.7 nm) deposited through incremental atomic layer deposition (ALD) cycles at the University of Wyoming.

❖The nanotube support made high-resolution TEM imaging of the supported Pt domains possible.

Mo_2C Nanotube, Pt ALD Preparation



Tan, S., et al. ACS Appl. Mater. Interfaces 2017, 9, 9815-9822.
Saha, S., et al. Mater. Chem. A, 2016, 4, 9253-9265.

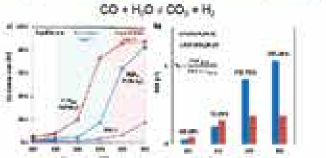
HRTEM images of (a) bare Mo_2C (100), (b) 15 ALD cyles of Pt on Mo_2C, (c) 50 Pt/Mo_2C and (d) 100 Pt/Mo_2C. The lattice fringes are in the direction of hexagonal Mo_2C (100) plane, Strain-ligand effect. (Tan, L., Saha, S., Li, D.)

Experiment

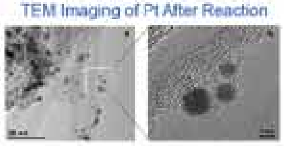
❖Conventional steady-state kinetic testing for water-gas shift chemistry indicates Pt/Mo_2C materials have enhanced performance.

Steady-State Testing: Water-Gas Shift (WGS)

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$



TEM Imaging of Pt After Reaction



❖Molybdenum oxidized, Pt reduced with pronounced carbon buildup

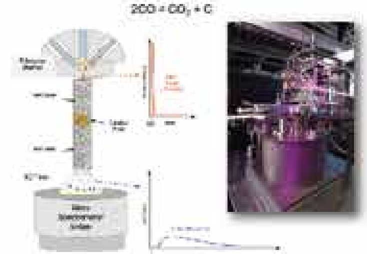
Temporal Analysis of Products (TAP)

❖Transient experiments of simple reactions can be used to better understand the global performance under steady-state conditions.

❖TAP pulse response experiments were used to monitor incremental changes in kinetic performance of Pt/Mo_2C materials used for water-gas shift reaction.

❖ CO disproportionation was used as a simple probe reaction.

$$2CO \rightleftharpoons CO_2 + C$$

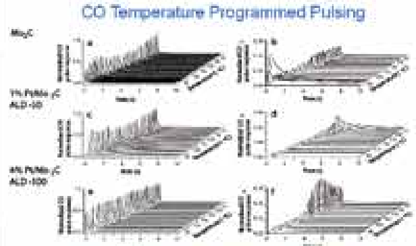


Features of TAP:
- Intrinsic, detailed kinetics of elementary reaction steps
- Separation of reactant inputs and product detection with high time resolution
- Isothermal operation even for highly exothermic reactions
- Pulse-by-pulse titration of materials
- Well-defined Knudsen transport

Analysis of Exit Flow Gives Intrinsic Characteristics
- Reaction Rate Constants
- Activation Energy
- Surface concentrations
- Surface Residence Time
- Number of Active Sites
- Concentration of Intermediates
- Surface to Bulk Migration Rate
- Complex, Multistep Microkinetic Models

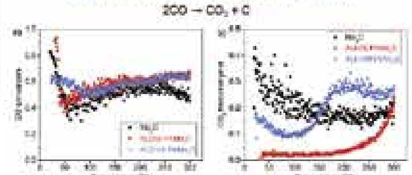
❖CO pulse response data of these materials demonstrated similar trends in conversion but significantly different trends for carbon storage and CO_2 evolution.

CO Temperature Programmed Pulsing



Conversion and Yield Temperature Trends

$$2CO \rightarrow CO_2 + C$$

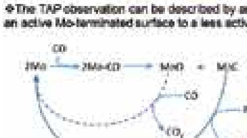


- Similar CO conversion behavior
- Turning point
  - Multiple steps with competing temperature dependences

- Markedly different CO_2 production
- Mo_2C deactivates
  - Pt stores CO at low temperature
  - Pt accelerates reaction at high T

Proposed Reaction Mechanism

❖The TAP observation can be described by an incremental transformation of an active Mo-terminated surface to a less active C-terminated surface

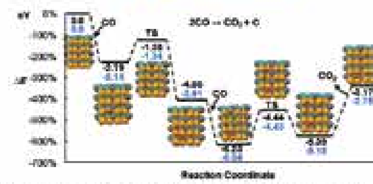


- Mo_2C produces CO_2
- Mo_2C Deactivates quickly
- Pt maintains active site by collecting C
- A 'carbon-spillover' mechanism

Theory - Computational Methods

- PBE GGA functional and PAW Pseudopotentials using VASP
- Meta GGA M06L static calculations with the optimized structures
- Optimized lattice constants:
  Mo_2C: 2a= 6.062 Å 2b= 6.0487 Å c= 4.706 Å; Pt: a = 3.976 Å
- Four slab layers with top two layers relaxed
- Vacuum Distance: 12 Å; E_{cutoff} = 520 eV
- Interface modeled by 12Pt@Mo_2C
- Climbing image nudged elastic band (cNEB) method for transition state search;
- Bader charge analysis for charger transfer.
  $E_{ads} = E_{slab\text{-}CO} - E_{slab} - E_{CO}$

Potential Energy Surface for CO Disproportionation on β-Mo_2C (100) Surface

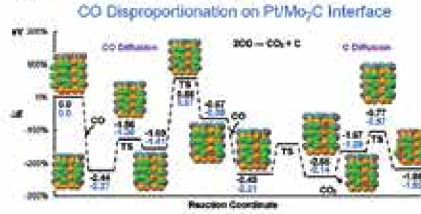


❖CO readily dissociates on Mo_2C and the remaining C atoms after CO_2 release deactivate the active Mo sites. O = Red.

Pt (111) Surface

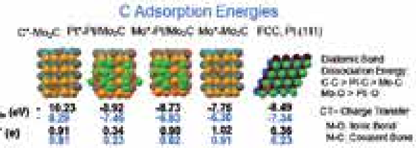
❖CO dissociation is endothermic by >4 eV, therefore unlikely

CO Disproportionation on Pt/Mo_2C Interface



The formation surface *-O still exothermic, but with a larger barrier energy, which indicates a high temperature to occur; The remaining C atoms after CO_2 release diffuse to Pt region and make Mo sites available for further reaction.

C Adsorption Energies



- Mo*-Mo_2C has lower surface energy (4.058 eV) compared to C*-Mo_2C (5.013 eV)
- CO adsorption takes place on both Mo_2C and Pt
- C*-Mo_2C and Pt are inactive for disproportionation
- Mo*-Mo_2C is most active for disproportionation
- Carbon prefers to migrate to Pt, Pt*-Pt/Mo_2C is most favorable.

Main Conclusions

- Pt-Mo_2C materials were tested with transient experiments of CO pulsing to better understand enhanced performance in global water-gas shift chemistry.
- From transient kinetic analysis and supporting DFT modeling a 'carbon spillover' mechanism is proposed where platinum acts to accumulate carbon which in turn prevents deactivation on the Mo_2C.
- A Pt-assisted carbon-spillover *microkinetic* mechanism is proposed to maintain Mo_2C global catalyst activity.
- These results give us new understanding for how catalysts can be made more active, energy efficient and durable under reaction conditions.

Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

PROJECT ID: 16-002

INL Initiative: Clean Energy Deployment

Dissolution of Carbonaceous Feedstocks Using Ionic Liquids

Ionic liquids (ILs) are salts that do not crystalize at room temperature; some have applications in energy. The objective of this project was to develop and demonstrate laboratory capabilities pertaining to an IL-based carbon-conversion process targeting coal and biomass feedstocks to enable a more-efficient utilization of regional fossil- and renewable-energy resources. ILs serve as a reaction medium that enables the dissolution and depolymerization of coal and biomass by disrupting intermolecular structures and carbon linkages. A key finding was that switchable ILs, which have improved separation capabilities relative to traditional ILs, can double the sugar released from biomass during enzymatic hydrolysis, which would increase ethanol yields from biochemical conversion. Future funding opportunities include long-term DOE programs, including the Bioenergy Technology Office's feedstock development, the National Energy Technology Laboratory's potential funding opportunity announcement on fossil-energy research and coal utilization, funding opportunities from the Advanced Research Project Agency—Energy program, State of Wyoming, and DOE Early Career Research Program (Basic Energy Science, Biological and Environmental Research). This project also generated the opportunity for partnerships with other national labs and industry.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): C. Luke Williams

INTERNAL COLLABORATORS (Idaho National Laboratory): Chenlin Li, Hongqiang Hu

EXTERNAL COLLABORATOR (University of Idaho): Haiyan Zhao

PUBLICATIONS:

Williams, C. L., C. Li, H. Hu, J C. Allen, and B. J. Thomas, "Three Way Comparison of Hydrophilic Ionic Liquid, Hydrophobic Ionic Liquid, and Dilute Acid for the Pretreatment of Herbaceous and Woody Biomass," *Frontiers in Energy Research* 6 (2018), p. 67.

PATENTS:

First filing: Li Chenlin, He Ting, C. Luke Williams, "Extraction of Rare Earth Elements and Carbon Rich Solids from Coal and Coal Byproducts Using Ionic Liquids," Attorney Docket No. S-147,940.

Idaho National Laboratory

Clean Energy Deployment -

Dissolution of Carbonaceous Feedstocks Using Ionic Liquids

C. Luke Williams, Chenlin Li, Hongqiang Hu, Haiyan Zhao (Univ. Idaho)

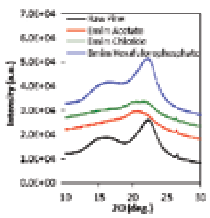
Project Objective:

This project focused on developing efficient ionic liquids based dissolution processes to transform the complex cross-linked macromolecular networks in biomass and coal into fuels and value-added chemicals. Achieving this goal will help address concerns around energy security and environmental sustainability.

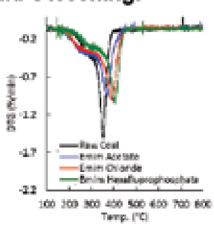
Research Approach:

This project started with screening ten traditional ionic liquids on a pine and subbituminous coal to understand the effects of each ionic liquid type. After screening, two unique ionic liquids were selected for testing a variety of coal and biomass samples to investigate dissolution extensibility. The final part of the project branched out to biomass dissolution with a unique class of "switchable" ionic liquids that would be more economically feasible to utilize on an industrial scale.

Results – Ionic Liquid Screening:



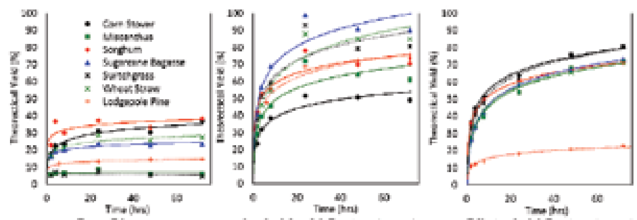
Ionic Liquids Disrupt Cellulose Crystallinity



Ionic Liquids Increase the Peak Combustion Temperature of Coal

- Hydrophilic ionic liquids work well for biomass dissolution while more hydrophobic ionic liquids work better for coal dissolution.
- No significant amounts of value added chemicals, such as asphaltenes, could be extracted from coal using ionic liquids.
- Ionic liquids with a strong hydrophobic anion, like PF_6, have the ability to complex with metals in biomass and coal. *This phenomena could be useful when extracting rare earth elements from coal fly ash.*

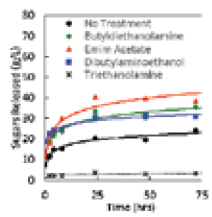
Results – Ionic Liquid Biomass Pretreatment Extensibility:



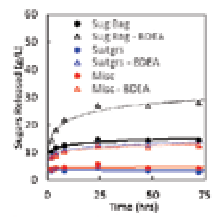
Raw Biomass | Ionic Liquid Pretreatment | Dilute Acid Pretreatment

- *Ionic liquids are particularly effective for woody biomass pretreatment* as compared to traditional dilute acid based methods.
- Dilute acid pretreatment is generally more consistent than ionic liquid pretreatment for herbaceous biomass.

Results – Switchable Ionic Liquids (SWIL):



Corn Stover with Various SWIL



SWIL Effect on Herbaceous Biomass

- *Switchable ionic liquids can double the natural sugar released from biomass during* enzymatic hydrolysis.
- Across a variety of biomass types switchable ionic liquids were about a quarter as effective as traditional ionic liquids but they cost over ten time less.

Research Outputs:

- This work has resulted in seven reports/posters, three conference presentations, one journal publication, and one US patent with three more publications in preparation.
- This work supported one masters student, Jared C. Allen, under Haiyan Zhao at the University of Idaho.
- This work was supported through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517 .

14 | interns worked on projects featured in this report

PROJECT ID: 16-176

INL Initiative: Clean Energy Deployment

Development of Direct Carbon Fuel Cells

Carbon is the main component of coal and biomass, and its conversion with high efficiency to power generation is always a key to low-carbon footprint. The goal of this project was to develop direct carbon fuel-cell technologies as a domestic clean energy source. The project leveraged capabilities of the Center for Advanced Energy Studies to build a new INL capability in energy conversion and distributed generation. The project focused on developing robust, reduced-temperature direct carbon fuel cells by integrating the expertise in coal or carbon engineering, ceramic fabrication and characterization, corrosion mitigation, system modeling, and integration with perovskite-carbonate composite electrolytes. A systematic approach was implemented to address materials and process aspects of green-coal utilization technology. This work is contributing to changes in the coal industry's paradigm, from combustion to electrochemical oxidation so that carbon can be used as a clean energy source. Simultaneously, a number of high-value chemicals were produced while direct carbon fuel-cell-grade carbon was extracted. This research promotes highly efficient energy conversion and a reduction of the carbon footprint in power generation. The principal investigator is working with industry and government to secure direct funding, based on this work.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Dong Ding

EXTERNAL COLLABORATOR: Maohong Fan (University of Wyoming); Haiyan Zhao (University of Idaho)

INTERNAL COLLABORATORS (Idaho National Laboratory): Ting He, Wei Wu, Yunya Zhang, Wenjuan Bian

PUBLICATIONS:

Lu, W. T. He, B. Xu, X. He, H. Adidharma, M. Radosz, K. Gasema, and M. Fan, "Progress in catalytic synthesis of advanced carbon nanofibers," *Journal of Materials Chemistry* A 27 (2017).

Tang, Q., Z. Shen, L. Huang, T. He, H. Adidharma, A.G. Russelle, and M. Fan, "Synthesis of methanol from CO2 hydrogenation promoted by dissociative adsorption of hydrogen on a Ga3Ni5(221) surface," *Physical Chemistry Chemical Physics* 28 (2017).

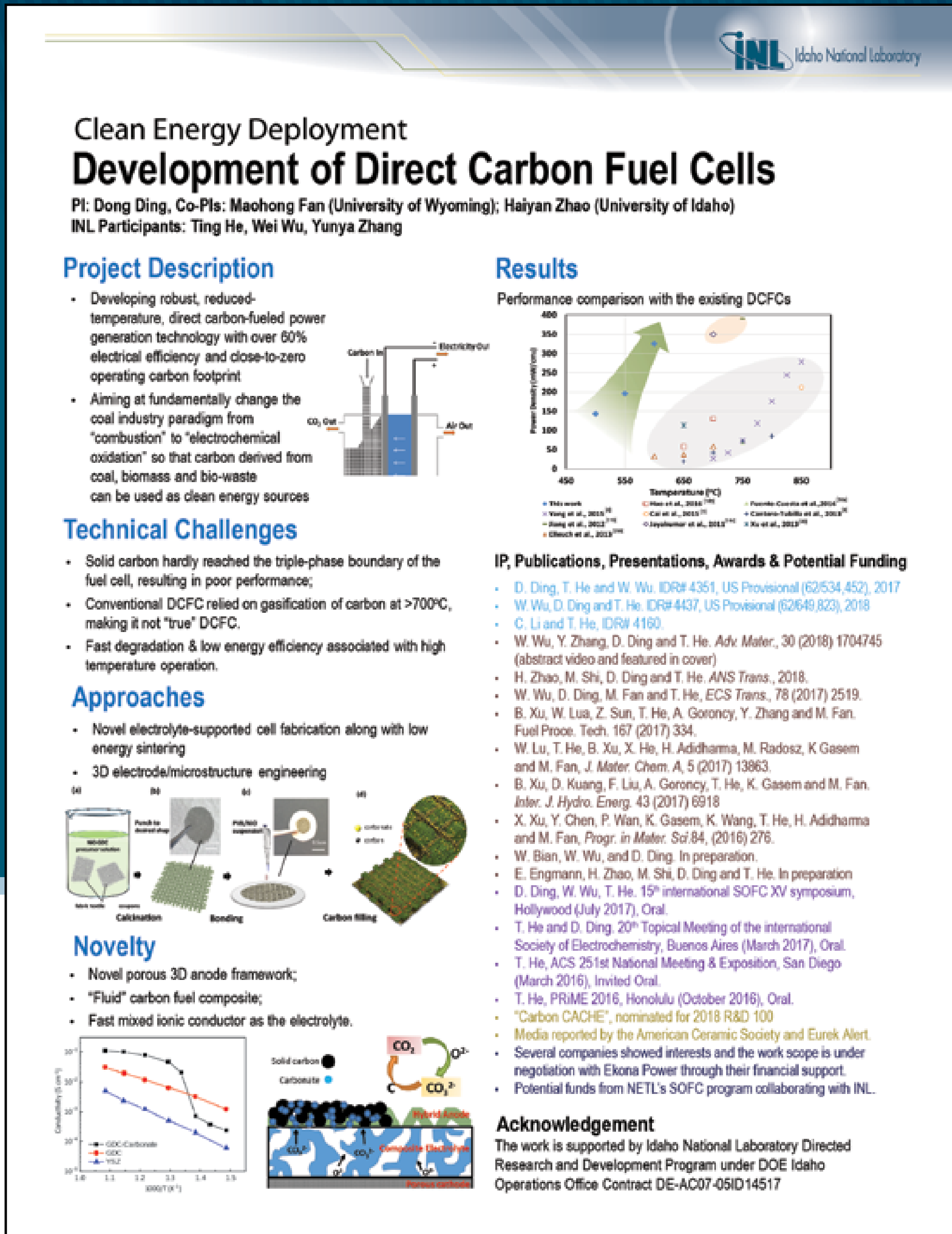
Wu, W., D. Ding, M. Fan, and T. He, "A High Performance Low Temperature Direct Carbon Fuel Cell Fuel Compatibility and Alternative Fuels," *ECS Transactions* 78.1 (2017), pp. 2519–2526.

Wu, W., Y. Zhang, D. Ding, and H. Ting, "A High-Performing Direct Carbon Fuel Cell with a 3D Architectured Anode Operated Below 600°C," *Advanced Materials* 30 (2018), pp. 1–6 (1704745, abstract video and featured on cover).

Xu, X., Y. Chen, P. Wan, K. Gasem, K., Wang, T. He, H. Adidharma, and M. Fan, "Extraction of lithium with functionalized lithium ion-sieves," *Progress in Materials Science* 84 (2016), pp. 276–313.

Xu, B., D. Kuang, F. Liu, A. Goroncy, T. He, K. Gasem, and M. Fan, "Characterization of Powder River Basin coal pyrolysis with cost-effective and environmentally-friendly composite Na-Fe catalysts in a thermogravimetric analyzer and a fixed-bed reactor," *International Journal of Hydrogen Energy* 43.14 (2017), pp. 6918–6935.

Xu, B., W. Lu, Z. Sun, T. He, A. Goroncy, Y. Zhang, and M. Fan, "High-quality oil and gas from pyrolysis of Powder River Basin coal catalyzed by an environmentally-friendly, inexpensive composite iron-sodium catalysts," *Fuel Processing Technology* 167 (2017), pp. 334–344.



PATENTS:

First filing: A provisional patent application, 62/534,452, "A High-Performance Low-Temperature Fuel Cell with an Architecture Anode Framework," filed 7/19/17, D. Ding, T. He and W. Wu. IDR# 4351, US Provisional (62/534,452), 2017. The provisional filing was not converted to non-provisional filing.

First filing: A provisional patent application, 62/649,823, "Electrochemical Cells Comprising Three-Dimensional (3D) Electrodes Including a 3D Architectured Material, Methods for Forming the 3D Architectured Material, and Related Methods of Forming Hydrogen," filed 3/29/18.

NUMBER OF INVENTION DISCLOSURE REPORTS: 2

PROJECT ID: 16-187

INL Initiative: Clean Energy Deployment

Micro-Scale Technique to Evaluate Grain Boundary Cohesion of Irradiated Alloys

Metallic alloys are widely used or planned for use as structural and cladding materials in current and future reactors. Under irradiation, grain-boundary cohesion strength decreases due to interaction with defects and impurities, leading to intergranular fracture and embrittlement of alloys. Work in this project involved developing a technique to quantify grain-boundary cohesion and its impact on fracture behavior in irradiated alloys by utilizing transmission electron microscopic in situ mechanical testing in concert with multiscale modeling. Molecular dynamics uniaxial tension simulations show that helium segregation at grain boundaries significantly weakens the strength of pure iron by promoting intergranular fracture. The transmission electron microscopic in situ mechanical testing was a novel approach for studying the real-time mechanical response of materials. The capabilities of transmission electron microscopic in situ mechanical testing and Multiphysics Object Oriented Simulation Environment based fracture models developed in this work will help elucidate and predict the materials' performance in reactors. In turn, it would enable the use of safer and more economical nuclear energy in the future.

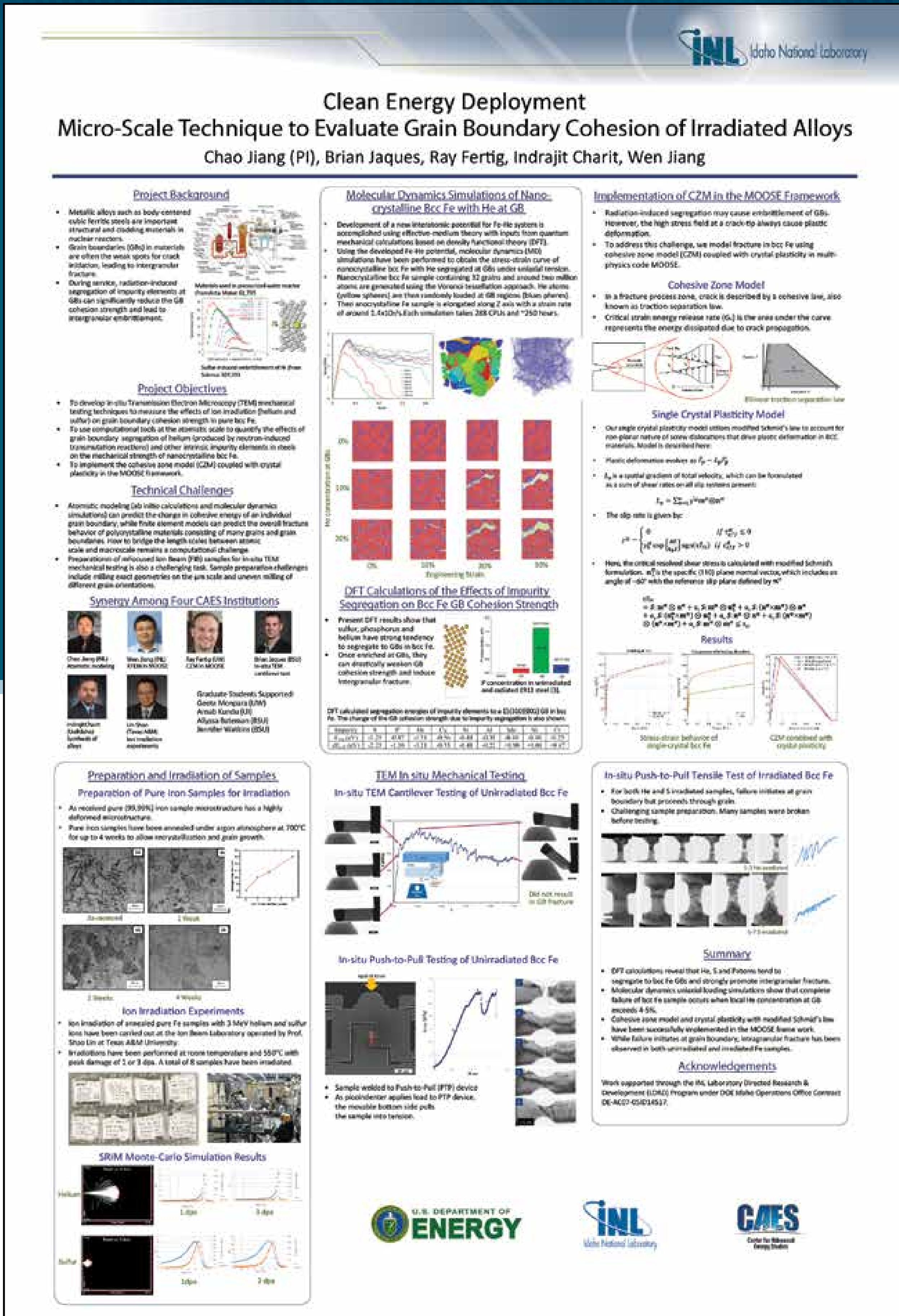
PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Chao Jiang

INTERNAL COLLABORATOR (Idaho National Laboratory): Wen Jiang

EXTERNAL COLLABORATOR (Boise State University): Brian Jaques

EXTERNAL COLLABORATOR (University of Wyoming): Ray Fertig

EXTERNAL COLLABORATOR (University of Idaho): Indrajit Charit


Idaho National Laboratory
Clean Energy Deployment
Micro-Scale Technique to Evaluate Grain Boundary Cohesion of Irradiated Alloys
Chao Jiang (PI), Brian Jaques, Ray Fertig, Indrajit Charit, Wen Jiang
Project Background
Metallic alloys such as body-centered cubic ferritic steels are important structural and cladding materials in nuclear reactors.
Grain boundaries (GBs) in materials are often the weak spots for crack initiation, leading to intergranular fracture.
During service, radiation-induced segregation of impurity elements at GBs can significantly reduce the GB cohesion strength and lead to intergranular embrittlement.
Project Objectives
To develop in-situ Transmission Electron Microscopy (TEM) mechanical testing techniques to measure the effects of ion irradiation (helium and sulfur) on grain boundary cohesion strength in pure bcc Fe.
To use computational tools at the atomistic scale to quantify the effects of grain boundary segregation of helium (produced by neutron-induced transmutation reactions) and other intrinsic impurity elements in steels on the mechanical strength of nanocrystalline bcc Fe.
To implement the cohesive zone model (CZM) coupled with crystal plasticity in the MOOSE framework.
Technical Challenges
Atomistic modeling (ab initio calculations and molecular dynamics simulations) can predict the change in cohesive energy of an individual grain boundary, while finite element models can predict the overall fracture behavior of polycrystalline materials consisting of many grains and grain boundaries. How to bridge the length scales between atomic scale and macroscale remains a computational challenge.
Preparations of refocused Ion Beam (FIB) samples for in-situ TEM mechanical testing is also a challenging task. Sample preparation challenges include milling exact geometries on the µm scale and uneven milling of different grain orientations.
Synergy Among Four CAES Institutions
Graduate Students Supported:
Molecular Dynamics Simulations of Nano-crystalline Bcc Fe with He at GB
Development of a new interatomic potential for Fe-He system is accomplished using effective-medium theory with inputs from quantum mechanical calculations based on density functional theory (DFT).
Using the developed Fe-He potential, molecular dynamics (MD) simulations have been performed to obtain the stress-strain curve of nanocrystalline bcc Fe with He segregated at GBs under uniaxial tension.
Nanocrystalline bcc Fe sample containing 32 grains and around two million atoms are generated using the Voronoi tessellation approach. He atoms (yellow spheres) are then randomly loaded at GB regions (blues spheres).
Engineering Strain
DFT Calculations of the Effects of Impurity Segregation on Bcc Fe GB Cohesion Strength
Present DFT results show that sulfur, phosphorus and helium have strong tendency to segregate to GBs in bcc Fe.
Once enriched at GBs, they can drastically weaken GB cohesion strength and induce intergranular fracture.
Implementation of CZM in the MOOSE Framework
Radiation-induced segregation may cause embrittlement of GBs. However, the high stress field at a crack-tip always cause plastic deformation.
To address this challenge, we model fracture in bcc Fe using cohesive zone model (CZM) coupled with crystal plasticity in multi-physics code MOOSE.
Cohesive Zone Model
In a fracture process zone, crack is described by a cohesive law, also known as traction-separation law.
Critical strain energy release rate (Gc) is the area under the curve represents the energy dissipated due to crack propagation.
Bilinear traction separation law
Single Crystal Plasticity Model
Our single crystal plasticity model utilizes modified Schmid's law to account for non-planar nature of screw dislocations that drive plastic deformation in BCC materials. Model is described here:
Plastic deformation evolves as
The slip rate is given by:
Results
Stress-strain behavior of single-crystal bcc Fe
CZM combined with crystal plasticity
Preparation and Irradiation of Samples
Preparation of Pure Iron Samples for Irradiation
As received pure (99.99%) iron sample microstructure has a highly deformed microstructure.
Pure iron samples have been annealed under argon atmosphere at 700°C for up to 4 weeks to allow recrystallization and grain growth.
As-received
1 Week
2 Weeks
4 Weeks
Ion Irradiation Experiments
Ion irradiation of annealed pure Fe samples with 3 MeV helium and sulfur ions have been carried out at the Ion Beam Laboratory operated by Prof. Shao Lin at Texas A&M University.
Irradiations have been performed at room temperature and 550°C with peak damage of 1 or 3 dpa. A total of 8 samples have been irradiated.
SRIM Monte-Carlo Simulation Results
Helium
Sulfur
1 dpa
3 dpa
TEM In situ Mechanical Testing
In-situ TEM Cantilever Testing of Unirradiated Bcc Fe
Did not result in GB fracture
In-situ Push-to-Pull Testing of Unirradiated Bcc Fe
Sample welded to Push-to-Pull (PTP) device.
As picoindenter applies load to PTP device, the movable bottom side pulls the sample into tension.
In-situ Push-to-Pull Tensile Test of Irradiated Bcc Fe
For both He and S irradiated samples, failure initiates at grain boundary but proceeds through grain.
Challenging sample preparation. Many samples were broken before testing.
Summary
DFT calculations reveal that He, S and P atoms tend to segregate to bcc Fe GBs and strongly promote intergranular fracture.
Molecular dynamics uniaxial loading simulations show that complete failure of bcc Fe sample occurs when local He concentration at GB exceeds 4-5%.
Cohesive zone model and crystal plasticity with modified Schmid's law have been successfully implemented in the MOOSE frame work.
While failure initiates at grain boundary, intragranular fracture has been observed in both unirradiated and irradiated Fe samples.
Acknowledgements
Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.
U.S. DEPARTMENT OF ENERGY
Idaho National Laboratory
CAES

PROJECT ID: 16-215

INL Initiative: Clean Energy Deployment

Electrochemical Manufacturing Processes

Enabling advanced manufacturing through process intensification in thermodynamics is challenging, but crucial to American manufacturing leadership and competitiveness. This project focused on the most energy-intensive activation process in manufacturing chemicals, plastics (synthetic polymers), and transportation fuels from natural gas and natural-gas liquids feedstocks. The goals of this project were to establish an electrochemistry platform, develop transformative electrochemical manufacturing processes that can revolutionize the energy-intense petrochemical industry, and implement large-scale nuclear-derived heat and renewable electricity in the industry. A systematic approach was implemented to develop electrochemical reactors that can use nuclear-derived heat and renewable electricity to convert natural gas and natural-gas liquids to olefins or alcohols for petrochemical-product manufacturing. This project aimed to change fundamentally the petrochemical manufacturing paradigm from widely used thermal practices (based on fossil energy) to a clean energy regime. The novel electrochemical processes developed will help advance small-modular-reactor deployment through market pull, particularly from manufacturing. A core electrochemical capability was established that can support and leverage programs such as hybrid energy systems, where the cogeneration of power and products is key to manage a large-scale renewable electricity grid and create the regional partnerships that are the stewards of enormous carbon reserves. This project has already led to direct funding from the Energy Environment and Renewable Energy.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Dong Ding

INTERNAL COLLABORATORS (Idaho National Laboratory): Ting He, Wei Wu, Yunya Zhang, Lucun Wang, Christopher Orme, David Rohrbaugh, Hanping Ding, Wenjuan Bian (Intern)

EXTERNAL COLLABORATOR: Wenzhuo Wu (Purdue University); Meng Zhou (New Mexico State University)

PUBLICATIONS:

Ding, D., Y. Zhang, W. Wu, D. Chen, M. Liu, and T. He, "A novel low-thermal-budget approach for the co-production of ethylene and hydrogen via the electrochemical non-oxidative deprotonation of ethane," *Energy & Environmental Science* 11.7 (2018), 1710-1716. (featured on cover).

He, T., P. Kar, N. McDaniel, and B. Randolph, "Electrochemical Hydrogen Production," in *Springer Handbook of Electrochemical Energy* (pp. 897-934). New York, New York: Springer.

Sun, K., D.M. Ginosar, T. He, Y. Zhang, M. Fan, and R. Chen, "Progress in Nonoxidative Dehydroaromatization of Methane in the Last 6 Years," *Industrial & Engineering Chemistry Research* 57.6 (2018), pp. 1768–1789.

Tang, Q., Z. Shen, L. Huang, T. He, H. Adidharma, A.G. Russell, and M. Fan, "Synthesis of methanol from CO_2 hydrogenation promoted by dissociative adsorption of hydrogen on a Ga3Ni5(221) surface," *Physical Chemistry Chemical Physics*, 19.28 (2017), pp. 18539–18555.

Wu, W., D. Ding, M. Fan, and T. He, "A High Performance Low Temperature Direct Carbon Fuel Cell Fuel Compatibility and Alternative Fuels," *ECS Transactions* 78.1 (2017), pp. 2519–2526.

Wu, W., D. Ding, and T. He, "Development of High Performance Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells," *ESC Transactions* 80.9 (2017), pp. 167–173.

Award Winner: First Place in INL Poster Competition

Wu, W., H. Ding, Y. Zhang, Y. Ding, P. Katiyar, P.K. Majumdar, T. He, and D. Ding, "3D Self Architectured Steam Electrode Enabled Efficient and Durable Hydrogen Production in a Proton Conducting Solid Oxide Electrolysis Cell at Temperatures Lower Than 600°C," *Advanced Science* (2018), p. 1800360. (Featured in front piece)

Xu, X., Y. Chen, P. Wan, K., Gasem, K., Wang, T. He. H. Adidharma, and M. Fan, "Extraction of lithium with functionalized lithium ion-sieves," *Progress in Materials Science* 84 (2016), pp. 276–313.

PATENTS:

First filing: D. Ding, L. Wang, Y. Zhang and T. He.. Elect for provisional filing (2018), "Composite Media for Non-Oxidative Ethane Dehydrogenation, and Related Ethane Activation Systems and Method of Processing an Ethane-Containing Stream," filed 7/16/18.

First filing: D. Ding, W. Wu and H. Ding, (2018). "Methods and Systems for Co-producing Hydrocarbon Products and Ammonia, and Related Electrochemical Cells," filed 8/6/18.

First filing: D. Ding, H. Ding, W. Wu, C. Jiang. IDR# 5662, Elect for provisional filing(2018) Provisional filing, application number 62/727,151, "Electrochemical Cells for Hydrogen Gas Production and Electricity Generation, and Related Structures, Apparatuses, Systems, and Methods," filed 9/5/18.

First filing: D. Ding, T. He, W. Wu and Y. Zhang, IDR# 4478, U.S. Provisional (2018). Application number 62/597,004, titled "Methods for Producing Hydrocarbon Products and Hydrogen Gas through Electrochemical Activation of Methane, and Related Systems and Electrochemical Cells," filed 12/11/17.

NUMBER OF INVENTION DISCLOSURE REPORTS: 5

PROJECT ID: 17A1-007

INL Initiative: Clean Energy Deployment

High Performance Polymeric Membranes for Nanofiltration Applications

Polymeric membranes are inherently energy-saving systems and may be retrofitted onto many existing unit operations because of their relatively small footprints and flexible designs. Lacking in many current membrane-based filtration systems is an ability to withstand aggressive feed streams, including high temperatures, organic solvents, and high or low pH. This project's goal was to develop new high performance polymeric membrane systems for a variety of filtration processes, including nanofiltration or ultrafiltration. The high-performance membranes thus developed improve processes for water treatment or chemical-product purification and enable aspects of existing processes and capabilities. The membranes incorporated materials that will increase hydrophilicity and improve liquid throughput and selectivity and membrane stability. The project is built upon high-performance polymer membrane capabilities at INL and developed new methods to introduce porosity that enables high flow rates in challenging water separations. The researchers are pursuing direct funding through the DOE Office of Energy Efficiency and Renewable Energy.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): John Klaehn

INTERNAL COLLABORATORS (Idaho National Laboratory): Birendra Adhikari, Christopher Orme, Joshua Kane, Aaron Wilson, Harry Rollins

EXTERNAL COLLABORATORS (University of California, Los Angeles): Xiaobo Zhu, David Jassby

High Performance Polymeric Membranes for Nanofiltration Applications (17A1-007FP)

[1]John R. Klaehn, [1]Birendra Adhikari, [1]Christopher J. Orme, [1]Joshua J. Kane, [1]Aaron D. Wilson, [2]Xiaobo Zhu and [2]David Jassby
[1]Idaho National Laboratory (INL), Idaho Falls, ID and [2]University of California at Los Angeles (UCLA), Los Angeles, CA

Objective

- Proof of principle to develop new high performance (HP) polymer membranes for a variety of filtration processes, including nanofiltration (NF), ultrafiltration (UF) through controlled hydrophilicity, porosity for high flow rates.
- The project is based on HP polymer membrane capabilities at INL, which develops methods to introduce porosity that will enable high water flux for challenging water purification applications.

Technical Challenges

- Most commercial polymeric membranes are not capable of handling high temperature liquid separations at or above 50 °C.
- Current state of the art high temperature separations is expensive where high temperature NF and UF presents an opportunity.

Approach

- Use a number of HP polymers including polybenzimidazole (PBI), polyimides, fluoropolymers, block co-polyamide and polyphosphazenes.
- Membrane designs focused on the nanostructured fugitive fillers (carbon nanotubes (CNT), ceramic particles, nanocrystalline cellulose (NCC)) to induce porosity.
- Test commercially available membranes at high temperature conditions (up to 85 °C).
- Prepare and characterize high temperature nanofiltration (HTNF) membranes with fillers.

Novelty

- INL has an extensive background on the development of HP polymers: PBI, VTEC (polyimides), Polyphosphazene, etc.

- UCLA uses a combination of CNTs with polymer binders for NF and UF membranes.
- UCLA membranes are electrically conducting for water treatment, which reduce fouling (organics and mineral scaling).
- INL and UCLA are implementing HP polymers to create new NF membranes that have greater temperature stability.

Results

- Several commercially available membranes were tested with red and blue dyes and 2000 ppm $MgSO_4$ solution.
- Membranes failed at or below 50 °C are
  - GE Osmonics CK
  - Snyder Flat Sheet membrane
  - Nanostone NF4
- Two membranes that maintained performance are
  - DOW FILMTEC NF90
  - DOW FILMTEC NF270

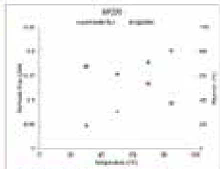


Figure 1. NF270 membrane performance

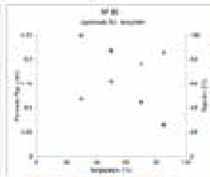


Figure 2. NF90 membrane performance

Figure 3. Membrane testing systems: Clam shell coupon testing (left) and Spiral wound/hollow fiber membrane module testing (right)

Membrane Characterization

Figure 4. SEM image (left) and general image of VTEC-EG/CNT membrane (right).

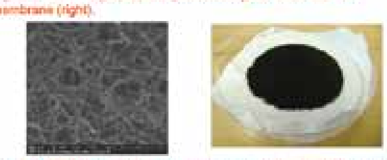


Figure 5. SEM image (left) and general image of PDMS/CNT membrane (right).

- These membranes show rejection of red dye (molecular weight cut off of 1370 g/mol) at temperatures as high as 80 °C.

Accomplishments

- **Publication:** Journal article submission to *Journal of Membrane Science, INL/CON-17-41157* "The role of water activity (aw) in water transport through membranes," under review.
- **Presentations:** Posters were given at the International Congress on Membranes and Membrane Processes (ICOM2017), 2017 INL Summer Intern Expo/Poster Session, and Gordon Research Conference (GRC 2018) for Membranes: Materials and Processes.
- **Collaboration:** Subcontract (#197743) with UCLA (David Jassby) to develop HP polymer CNT NF membranes.
- Science Undergraduate Laboratory Internship (SULI): Joseph M. Barnes worked on water chemical potential using polyethylene glycols.
- *INL/CON-17-41160:* "Dewatering High Osmotic Potential Produced Water Using SPS FO," C.J. Orme (presenting), B. Adhikari, J.R. Klaehn, A.D. Wilson.
- *INL/CON-17-41111:* "Gas Permeability of Mix Matrix Phosphazene Polymer Blends," C.J. Orme (presenting), J.R. Klaehn, A.D. Wilson, J.S. McNally, J.J. Kane.
- *INL/CON-17-42717:* "The role of water activity (aw) in water transport through membranes," A.D. Wilson (presenting); J.R. Klaehn; C.M. Hrbac; C.J. Orme; D.L. Daubaras.
- *INL/MIS-17-42732:* "Investigation of the material osmotic density of aqueous poly (ethylene glycol) solutions," J. M. Barnes (SULI Intern, presenting); J.R. Klaehn, A.D. Wilson.
- *INL/CON-18-46006:* "High Performance Polymeric Membranes for Nano and Ultrafiltration Applications," B. Adhikari (presenting), C.J. Orme, J.R. Klaehn, A.D. Wilson, X. Zhu (UCLA), D. Jassby (UCLA).

Opportunities

- This technology fits into the Advanced Manufacturing platform where industrially critical chemical separations are sought. Further, there are new initiatives within DOE for cross-cutting platforms on energy and water, such as the expected water hub.
- Continue collaboration with UCLA to pursue new funding opportunities on membrane separations.

Acknowledgement

Work supported through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

PROJECT ID: 18A12-203

INL Initiative: Clean Energy Deployment

Optimization of Carbon Nanotubes in an Aluminum Matrix for Light-weighting Automobile Structures

Carbon nanotubes (CNTs) in metal matrix composites (MMCs) are promising materials for use in aerospace, energy, and automotive materials due to their enhanced mechanical, thermal, and electrical properties over the base metal. For the automotive industry, the increased strength allows for new designs that decrease the overall weight of the vehicle and thereby increase fuel efficiency. Although CNT MMCs hold great promise for lessening weight, they have yet to break into automotive applications due to engineering issues with CNT adhesion and dispersion within the metal matrix. This work sought to improve CNT dispersion within aluminum-matrix CNT MMCs and yield a better understanding of the underlying mechanisms, contributing to their enhanced properties. Effects of induction-melting and casting methods on the dispersion of CNTs were examined, though additional work is needed to ensure the dispersion of the CNTs through use of techniques such as nickel plating. In future work, researchers hope to explore the novel use of prestructured CNT foam to create the MMCs and the effects of CNT diameter and CNT length on CNT adhesion and mechanical properties.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Michael McMurtrey

INTERNAL COLLABORATORS (Idaho National Laboratory): Joshua Kane, Austin Matthews

Optimization of carbon nanotubes in an aluminum matrix for light-weighting automobile structures

M. McMurtrey, J. Kane, A. Matthews

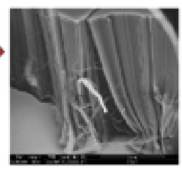
CED: Advanced Manufacturing 2.1.3, LDRD 18A12-203

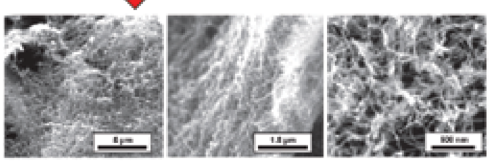
Background/Objective

Carbon nanotubes (CNT) in metal matrix composites (MMC) exhibit improved mechanical, thermal, and electrical properties over the base metal. For the automotive industry the increased strength allows for new designs that decrease the overall weight. Although CNT-MMCs hold great promise for light weighting, they have yet to break into automotive applications due to engineering issues with CNT adhesion and dispersion within the metal matrix. This work seeks to improve CNT dispersion/adhesion within aluminum matrix CNT-MMCs.

Methods for improving dispersion/adhesion

- Ultra-long CNTs
- Induction melting/casting
- Metal (nickel) plating of CNTs
- Pre-structured CNT foam





Induction casting

Centrifugal caster

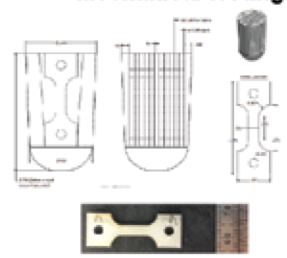
Metal is heated by induction coils inducing currents through the metal

Three forms of aluminum were tested

- Weld wire
- Granules (~1 mm)
- Pellets (~5 mm)

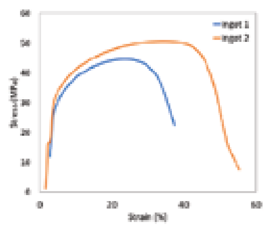
Induction heating chosen for better CNT dispersion due to natural mixing from the eddies caused by induced currents

Mechanical testing and characterization



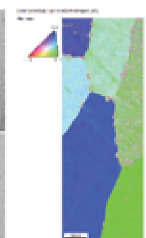
Specimen machining plan from cast ingot and final specimen

Mechanical test frame



Mechanical results (pure aluminum)
Expected yieldstrength: ~50 MPa
Expected tensile strength: ~65 MPa

Optical images of etched microstructure: Ingot 1 (top), Ingot 2 (bottom)



EBD scans of early ingot

Technical challenges

A number of challenges were associated with casting aluminum

- During machining, cut layers would curl, specimens contained damage prior to mechanical testing
  - Heat treatment did not improve
  - Larger metal source did not improve
  - Fixed by addition of fluxes and longer melt times
- Poor results attempting to include CNTs
  - Possible fixes include nickel plating
  - Pre-structured CNTs (foam)

PROJECT ID: 16-081

INL Initiative: Critical Infrastructure Protection

Modeling Thermite Reactions

Devices that use thermite-type energetic materials have many potential applications within Homeland Security as well as commercial applications. The goal of this project was to increase the understanding of reaction rate and dynamics of thermites using Multiphysics Object Oriented Simulation Environment (MOOSE), a finite–element-based framework that can be used to solve complex systems of coupled, nonlinear partial differential equations. MOOSE has not yet been applied to the study of energetic-material combustion, and little science underlies the understanding of thermites use and handling. The safe handling and use of thermites would be greatly improved if reactions could be modeled. Within this LDRD project, we successfully developed a thermite model that consists of coupled nonlinear thermal-thermal conduction partial differential equations and an Arrhenius type first-order kinetic thermite reaction model, using MOOSE framework. This MOOSE-based thermite model allowed us to improve understanding of the underlying science in the area of energetic materials combustion, and enable systematic study of nonlinear interactions between the thermal-diffusion process and reaction kinetics within thermite composites, which ultimately governs the propagation speed of the reaction front within thermite. The successful development of the thermite model based on MOOSE framework, validated by experiments, will significantly contribute to the enhancement of the experimental thermite research capabilities within INL's Homeland Security Directorate and attract external funding from the Department of Homeland Security.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Hai Huang

INTERNAL COLLABORATORS (Idaho National Laboratory): Jing Zhou, Bryon Curnutt, Ron Heaps

EXTERNAL COLLABORATORS (Texas Tech University): Michelle Pantoya, Ryan Bratton

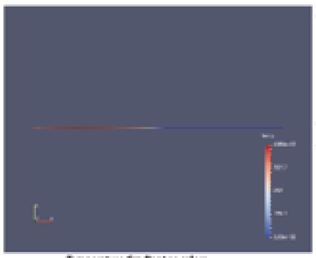
PUBLICATIONS:

Zepper, E. T., M. L. Pantoya, S. Bhattacharya, J. O. Marston, A. A. Neuber, and R. J. Heaps, "Peering through the flames: imaging techniques for reacting aluminum powders," *Applied Optics* 56.9 (2017), pp. 2535–2541.

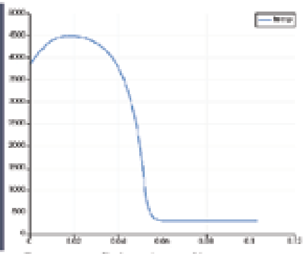
Idaho National Laboratory

Modeling Thermite Reactions

National Impact: This modeling capability will enhance the development and delivery of innovative and effective specialty devices capable of directing high energy in a rapid and controlled manner for military, protective force and emergency response. Being able to work with these materials in a computer model will increase the efficiency of development as well as provide an increase in safety and understanding.



Temperature Gradient as colors



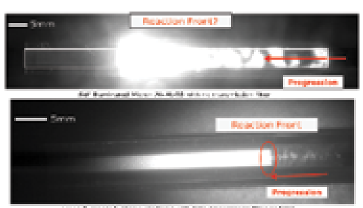
Temperature profile (x axes in seconds)

This figure shows output from the thermite reaction model. This model is a 2D model compact made of a mesh 2X100 units. Each graph shows the same moment in time of the reaction expressed as a specific term.
For example the two top graphs depict overall reaction temperature in different ways. The top left graph shows the temperature gradient as colors. The time slice is about halfway in the thermite compact. The red side has reacted, the blue side has not yet reacted. The reaction front is moving from left to right. The next graph to the right shows a plot of the temperature profile over time.

This Research is focused on understanding and documenting thermite reaction physics and chemical kinetics through the development of a Multiphysics Object Oriented Simulation Environment (MOOSE) application. MOOSE is a computer simulation tool developed at INL. The development of a MOOSE application may help increase the understanding of how thermites work and will enhance the use and efficiency of thermites. Safety and development efficiency should increase by having initial work being done in a simulated environment rather than having to run a set of experiments. When a thermite composition reacts, a great amount of heatis released along with solid, liquid, or gas reaction products. This model takes into account the thermodynamics of the reaction including phase changes that occur in the materials as they react. Working in a simulated environment protects the researcher from these hazards.

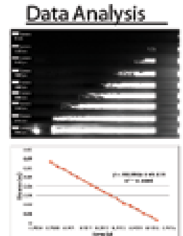
Experimental results are used to verify the model. Linear compacts are produced and reacted. Data is captured using high cameras as well as collected using DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) thermoanalytical techniques. The reaction gives off enough light that it can overwhelm the optical sensor and make it difficult to image. A method was developed to clearly see the reaction front. A copper vapor laser (CVL) is used to Illuminate the reaction front and a set of optical filter is also used to be able to see the reaction front clearly. The reaction velocity is then measured off of the video. This has been done manually as well as developing a video processing program to automate the procedure.

Self Illumination vs. CVL Illumination



- Reaction front is not clearly observed when imaging reactions using light emitted from reaction but is clearly observed with CVL illumination
- Observing and tracking the reaction front is enhanced and allows accurate a flame speed measurement

Data Analysis



- Manually track reaction front using recorded video and video playback software (Phantom Camera Controller)
- Export tracked points and plot distance vs. time
- Extract flame speed from the slope of the best fit line

Developing a MOOSE application to simulate thermite reactions will have the following benefits:

1. **Increased safety** – The researcher can simulate the use of thermite without being exposed to the potential hazards.
2. **Reduced Cost** – Development and use costs are realized when simulating under the MOOSE framework. A strength of MOOSE is that portions of the model canbeadded or modified without having to recompile. It is also modular in that bits of existing physics elements can be coupled together saving time in programming. New physics elements can be added as they are defined.
   Experiments can be run in a simulated environment quicker, cheaper. There is also a savings associated with not having to deal with the cost of potential safety hazards.
3. **Basic Science** – This will provide a greater understanding of these types of reactions. This innovative solutio will increase the understanding, performance and efficiency when using these materials.
4. **INL Recognition** – A number of papers will be published and will present INL and Texas Tech. as a leader in this field.

Development Plan:
An application was developed to run under the MOOSE framework. Starting with an existing finite element model that will be converted to run under MOOSE. When the model is verified and as understanding increases, then additional reaction physics will be added. As the model is developed results will be compared to empirical experimental data.

TEXAS TECH UNIVERSITY College of Engineeri

A collaboration between INL and Texas Tech University (TTU)
INL – Hai Huang, Jing Zhou, Bryon Curnutt, Ron Heaps
TTU – Dr. Michelle Pantoya, Ryan Bratton

Funded by INL LDRD Office :16-081

PROJECT ID: 16-085

INL Initiative: Critical Infrastructure Protection

Production of Fluoroanion Targets for AMS

Detection of nuclides of the actinide elements is critical for verifying the compliance of nuclear facilities with international nuclear-nonproliferation treaties. Current analysis methods require time-consuming and expensive sample preparation to achieve results acceptable to decision makers. Future analytical performance with markedly improved accuracy, precision, sensitivity and faster sample throughput will be required to keep up with an increasingly complex nuclear-proliferation environment. Accelerator mass spectrometry (AMS) offers an order-of-magnitude increase in sensitivity for actinide analysis, but the current state-of-the-art still requires exacting separations, limiting throughput, and is constrained in abundance sensitivity and precision. The objective of this project was to develop the technology for rapid production of sample targets for actinide analysis using AMS through the use of actinide fluoroanion salts produced using novel fluorinating ionic liquid and extracted using supercritical carbon dioxide. Actinide analysis using fluoroanion salts increased sensitivity and precision through the elimination of oxygen isobars. Additionally, manipulation of the degree of fluorination offered the potential for actinide separation in the ionization source, further reducing the need for chemical separation. This project produced novel methods for the rapid analysis of actinides using AMS, increasing the nation's capabilities in nuclear nonproliferation. Further research will focus on applying fluoroanion chemistry to sample preparation for other actinide-detection techniques, such as inductively-coupled plasma mass spectrometry.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Christopher Zarzana

INTERNAL COLLABORATORS (Idaho National Laboratory): Gary Groenewold, Michael Benson

EXTERNAL COLLABORATORS (Radbaud University): Jonathan Martens, Jos Oomens

EXTERNAL COLLABORATOR (Kyoto University): Rika Hagiwara

PUBLICATIONS:

Zarzana, C. A., G. S. Groenewold, M. T. Benson, J. E. Delmore, T. Tsuda, and R. Hagiwara, "Production of Gas-Phase Uranium Fluoroanions Via Solubilization of Uranium Oxides in the [1-Ethyl-3-Methylimidazolium]+[F(HF)2.3]– Ionic Liquid," *Journal of The American Society for Mass Spectrometry* (2018).

Idaho National Laboratory

Production of Fluoroanion Targets for AMS

Christopher A. Zarzana[a], Gary S. Groenewold[a], Michael T. Benson[a], Jonathan Martens[b], Jos Oomens[b], and Rika Hagiwara[c]

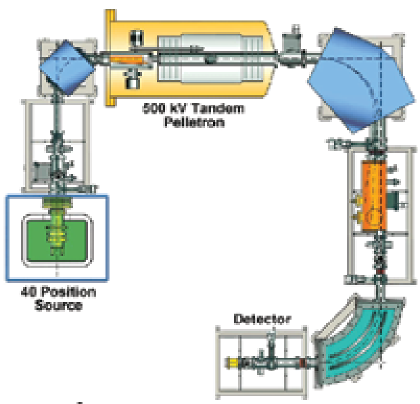
a) Idaho National Laboratory, USA; b) FELIX Laboratory, Radbaud University, Netherlands; c) Kyoto University, Japan

Impact

- Assure the peaceful use of nuclear energy by increasing the confidence of actinide isotope measurements used by nuclear nonproliferation treaty organizations.

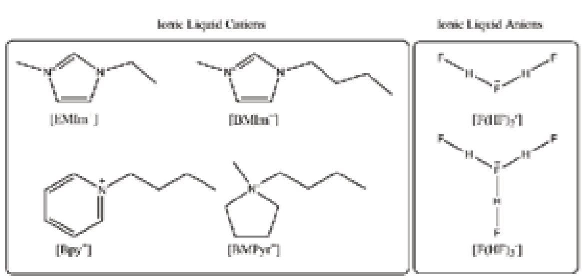
Objective

- Develop sample preparation methods that produce actinide fluoroanio salts targets for accelerator mass spectrometry (AMS) isotope-ratio measurements
- Elimination of isobaric interferences (^{18}O in particular)
- Lower cost and simplified sample preparation
- High efficiency ion formation



Approach

- Generate fluoroanions (e.g. UF_6^-) utilizing fluorinating ionic liquids (ILs)
  - Develop comprehensive understanding of IL – UF_6^- binding to guide optimization of ion production: *IR of discrete complexes + density functional theory*

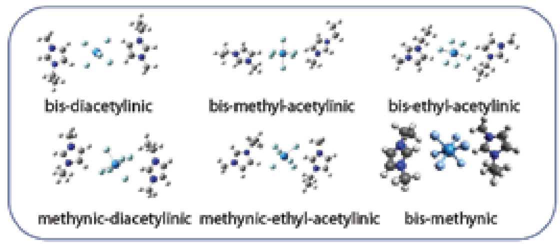


- Produce solid targets for the accelerator mass spectrometer via:
  - Precipitation of cation/fluoroanion salt
  - Super critical CO_2 extraction with ion pairing agent

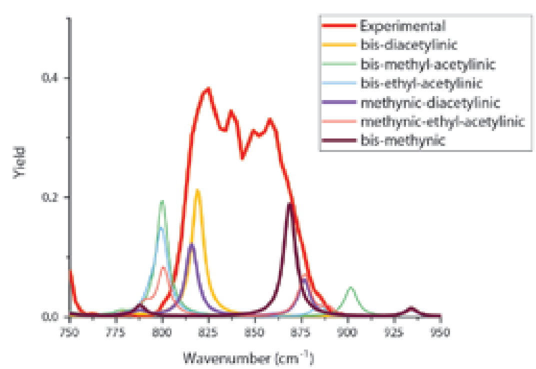
Results

IR of cation-metal fluoride complexes

- Quantum chemistry calculations suggest 6 possible gas -phase structures for these clusters with minimal energy differences:



- Gas-phase infrared multiphoton dissociation (IRMPD) measurements of the $[(EMIm)_2UF_6]^+$ cluster at the FELIX laboratory, Radbaud University, Netherlands compared to theoretical IR spectra from quantum chemistry calculations suggests a mixture of the bis-methynic (lowest calculated energy), *bis*-diacetylinic, and methynic-diacetylinic structures.



- This suggests the UF_6^- fluoroanion interacts more6 strongly with the protons on the imadizolium ring than those on the side chains. Overall, the interaction with the cation is weak, which suggests a strong ion pairing reagent will be effective for extracting UF_6^- from the ionic liquid.

Conclusions and Prospects

- The ionic liquid cation and fluoroanions interact in structure-directed ways
- The nature of the interaction should be tunable by adjusting ionic liquid cation structure
- Ion-pairing extraction looks promising for producing solid AMS targets

PROJECT ID: 16-098

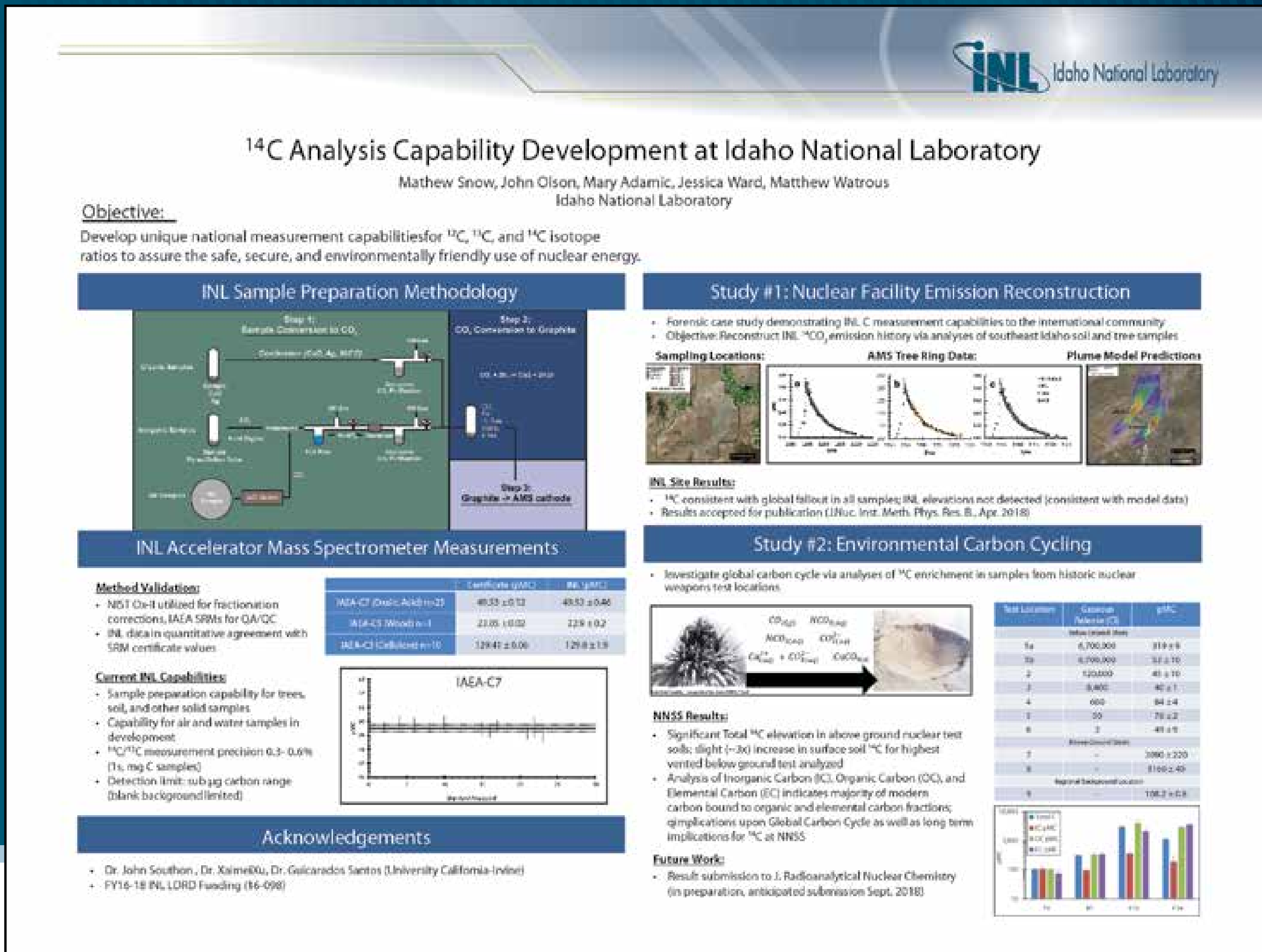
INL Initiative: Critical Infrastructure Protection

Carbon-14 Analysis Capability Development at Idaho National Laboratory

Carbon-14 (^{14}C) is an important isotope for developing efficient and sustainable energy source; analyses of ^{14}C from the environment provide critical insights into various processes, including global carbon cycling, environmental emissions from anthropogenic nuclear activities, and anthropological/archeological research activities (e.g., radiocarbon dating). The objectives of this research are to develop and demonstrate the capability of more sensitive and accurate methodologies to measure ultra-trace ^{14}C within samples analyzed for environmental measurements. Under this LDRD, the INL team developed techniques for ^{14}C analysis of inorganic, organic, and air samples. INL measurement sensitivities and precision were improved from 2% (1s) at 1 mg carbon load size down to < 0.5% (1s) at the 10 µg carbon load size using standard graphitization/solid accelerator mass spectrometry cathode-packing methods as a result of this research. Sample preparation and measurement capabilities on various environmental matrices were demonstrated in two separate published case studies: 1) analysis of tree and soil samples collected on and around the INL desert (evaluating perturbations in the local ^{14}C content due to historic INL reactor and reprocessing operations) and 2) analysis of soil samples taken from the Nevada National Security Site (assessing ^{14}C partitioning into the Nevada site local environment and differences in the chemical partitioning to inorganic (e.g., soil carbonates), organic, and elemental carbon constituents as a function of below- and above-ground nuclear tests, with implications on the global carbon cycle). The research was conducted in collaboration from scientists at the University of California at Irvine and with support from Brigham Young University-Idaho.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Mathew Snow

INTERNAL COLLABORATORS (Idaho National Laboratory): John Olson, Mary Adamic, Jessica Ward, Matthew Watrous, Darin Snyder


Idaho National Laboratory
14C Analysis Capability Development at Idaho National Laboratory
Mathew Snow, John Olson, Mary Adamic, Jessica Ward, Matthew Watrous
Idaho National Laboratory
Objective:
Develop unique national measurement capabilitiesfor 12C, 13C, and 14C isotope ratios to assure the safe, secure, and environmentally friendly use of nuclear energy.
INL Sample Preparation Methodology
Step 1: Sample Conversion to CO2
Step 2: CO2 Conversion to Graphite
Step 3: Graphite -> AMS cathode
INL Accelerator Mass Spectrometer Measurements
Method Validation:
NIST Ox-II utilized for fractionation corrections, IAEA SRMs for QA/QC
INL data in quantitative agreement with SRM certificate values
Current INL Capabilities:
Sample preparation capability for trees, soil, and other solid samples
Capability for air and water samples in development
14C/12C measurement precision 0.3- 0.6% (1s, mg C samples)
Detection limit: sub µg carbon range (blank background limited)
IAEA-C7
Acknowledgements
Dr. John Southon, Dr. XaimeiXu, Dr. Guicarados Santos (University California-Irvine)
FY16-18 INL LORD Funding (16-098)
Study #1: Nuclear Facility Emission Reconstruction
Forensic case study demonstrating INL C measurement capabilities to the international community
Objective: Reconstruct INL 14CO2 emission history via analyses of southeast Idaho soil and tree samples
Sampling Locations:
AMS Tree Ring Data:
Plume Model Predictions
INL Site Results:
14C consistent with global fallout in all samples; INL elevations not detected (consistent with model data)
Results accepted for publication (J.Nuc. Inst. Meth. Phys. Res. B., Apr. 2018)
Study #2: Environmental Carbon Cycling
Investigate global carbon cycle via analyses of 14C enrichment in samples from historic nuclear weapons test locations
Test Location
pMC
NNSS Results:
Significant Total 14C elevation in above ground nuclear test soils; slight (~3x) increase in surface soil 14C for highest vented below ground test analyzed
Analysis of Inorganic Carbon (IC), Organic Carbon (OC), and Elemental Carbon (EC) indicates majority of modern carbon bound to organic and elemental carbon fractions; qimplications upon Global Carbon Cycle as well as long term implications for 14C at NNSS
Future Work:
Result submission to J. Radioanalytical Nuclear Chemistry (in preparation, anticipated submission Sept. 2018)

PROJECT ID: 16-106

INL Initiative: Critical Infrastructure Protection

Industrial Control Systems - Cyber-attacks and Their Physical Effects

Understanding the physical impacts of a cyber-attack on an industrial control system network has proven to be difficult to quantify. Developing a non-subjective and consistent methodology helped to expand and improve the nation's capability to identify and understand the cascading physical impacts of a cyber-attack by determining functional consequence. These consequences can be applied across the component, system, industry, and dependent infrastructures. This project then took a novel approach in defining a cumulative operational consequence score that is based on the integration of cyber-induced physical consequence with the full dependency chain, allowing comparisons of the relative importance of critical infrastructure. A library of infrastructure-specific process maps and key data points was developed to support data collection that can be applied to specific infrastructure. This work is currently being integrated into a core capability that will be used to model the Ukraine electric-grid attack and is also being actively briefed to potential sponsors.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Mary Klett

INTERNAL COLLABORATORS (Idaho National Laboratory): Tim Klett, Dale Christiansen

Idaho National Laboratory

ICS-CAPE

Industrial Control Systems Cyber Attacks and their Physical Effects

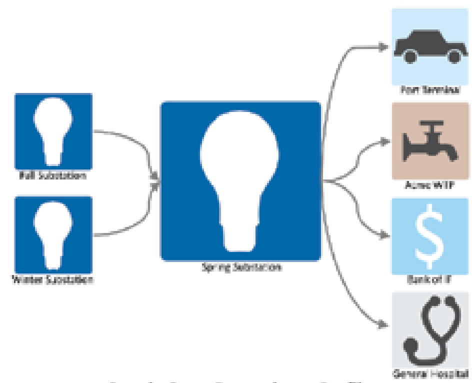
Mary Klett (PI) and Tim Klett

INL/MIS-17-42345

National Significance

Expands and improves the Nation's capability to identify and understand the cascading physical impacts of a cyber attack on an industrial control system (ICS) network.

- Data points at both a general and industry specific level will be collected for an ICS network to calculate the functional consequences of an attack as well as serve as a repository for other information needed for external modeling and analysis.
- The consequences will be applied across the component, system, industry, and dependent infrastructures.



Steady-State Dependency Profile

Technical Significance

Diving in to the innerworkings of a component/system/asset enables a robust assessment of a specific facility or collection of industry assets.

- Leveraged existing all-hazards analysis technologies, developed within an INL LDRD (14-093), for dependency analysis
- Expanded framework to allow for alibrary of industry specific network mapping profiles
- Allows analysis to be conducted within a facility and then taken one level up to identify potential impacts to supported infrastructure resulting in a cumulative consequence
- Leads to a more accurate understanding of the potential functional consequence of a cyber attack on an ICS network

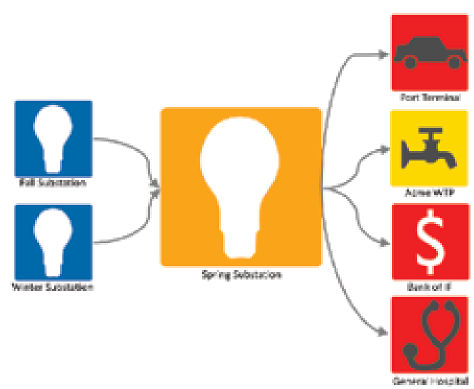
Network Mapping Profile Showing Functional Consequence

Innovative Aspects

This research will assess and enhance the use of a universal model and learning algorithms to delve into the components typically used within an industry and allow for flexibility and updating of libraries as additional data leads toidentification of new or updated base models.

Planners and threat analysts will have the opportunity to perform detailed evaluation of the impact of an attack or failure of a specific asset.

- The universal model will allow for rapid analysis of metrics and identify concrete consequences of a cyber attack.
- The enhanced understanding of the potential cascading impacts of a cyber attack on a specific component or asset will lead to more resilient designs.
- The relationship concerning structural complexity and it's impact to functional consequence and resilience is being analyzed.



Dependency Profile Showing Cascading Impacts

University of Idaho

Research supports INL employee's pursuit of PhD from the University of Idaho

ILLINOIS
INFORMATION TRUST INSTITUTE

Collaboration with the Information Trust Institute Is leading to robust algorithms

PROJECT ID: 16-129

INL Initiative: Critical Infrastructure Protection

Application of Radioactive Tracer Dilution Technique on Determination of Molten Salt Mass in Containers with Irregular Shape

Measuring the molten-salt mass in an electrorefiner is a critical step in safeguarding electrochemical recycling processes through nuclear-material accountancy. Researchers investigated the application of a radioactive-isotope dilution technique to determine molten-salt mass for electrochemical recycling and developed a technology for nuclear-material accounting with good measurement accuracy. This new technology can be used by the International Atomic Energy Agency to effectively and efficiently safeguard the electrochemical recycling plants of its member states. Researchers also developed measurement technology to determine the molten-salt mass. This work contributes a new safeguards measurement for electrochemical recycling. This research was the first time the technique was used in electrochemical recycling for the purpose of nuclear-material accountancy and for advancing international safeguards techniques.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Shelly Li

INTERNAL COLLABORATOR (Idaho National Laboratory): Jeff Sanders

EXTERNAL COLLABORATOR (The Ohio State University): Lei Cao

PUBLICATIONS:

Cao, L., J. Jarrell, A. Kauffman, S. White, K. Herminghuysen, D.E. Hardtmayer, and S. Li, "A Radioactive Tracer Dilution Method to Determine the Mass of Molten Salt," *Journal of Radioanalytical and Nuclear Chemistry* 314.1 (2017), pp. 387–393.

Hardmayer, D., K. Herminghuysen, S. White, A. Kauffman, J. Sanders, S. Li, and L. Cao, "Determination of molten salt mass using ^{22}Na tracer mixed with ^{154}Eu and ^{137}Cs," *Journal of Radioanalytical and Nuclear Chemistry*, Published online (03 July 2018), pp. 1–7.

PATENTS:

First filed: A Patent 'System for Determining Molten Salt Mass and related Methods," filed on Apr. 2, 2018 (PCT/US/18/25633).

Idaho National Laboratory

Application of Radioactive Tracer Dilution Technique on Determination of Molten Salt Mass in Containers with Irregular Shape

LDRD: 16-129
N&HS

Principal Investigator: Shelly X. Li (INL C400)
Co-investigator: Jeff Sanders (INL D230)
Collaborator: Dr. Lei Cao, The Ohio State University

Objective

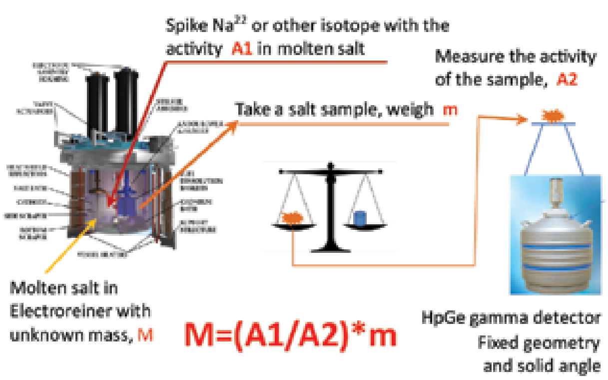
To develop a technical solution for nuclear material accountancy in high temperature molten salt such as molten salt reactors and pyroprocessing to treat used fuel

Background and motivation

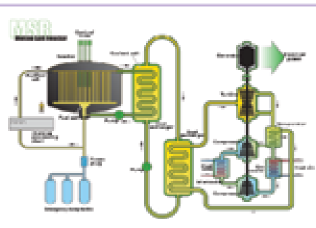
- Measuring the molten salt mass in a container is a critical step to safeguard pyroprocessing facilities and molten salt reactors
- The innovative process, when proven, will lead to acceptable safeguard options for the International Atomic Energy Agency and member states to reduce uncertainty in nuclear material inventories.

Approach

- A radioactive isotope with known radioactivity is spiked into the molten salt electrorefiner vessel
- After the salt is well mixed, a salt sample is taken and weighed.
- The radioactivity of the isotope within the sample is measured.
- The total salt mass in the electrorefiner vessel is calculated from the sample weight and radioactivity of the spike in the sample



The figure shows a schematic of proposed radioisotope dilution technique to determine molten salt mass in electrorefiner of pyroprocessing.The same technique can be applied to determine salt mass in molten salt reactors



Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

Highlights of Accomplishments

- Na^{22} has been demonstrated as an effective radioactive tracer
- Proof-of-concept measurements on a Na^{22} spiked salt with simulant fission products was successfully completed at The Ohio State University

Intellectual Properties

- An Invention Disclosure Record BA-887 was filed on January 2016
- A provisional patent application was filed in April 2017 by the INL titled" Radioactive Tracer Dilution Technique for Determining Molten Salt Mass."
- A Patent 'System for Determining Molten Salt Mass and related Methods" was filed on Apr. 18, 2018 (PCT/US/18/25633)

Journal Publications

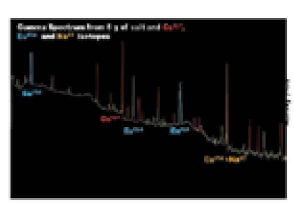
- D. Hardmayer, K. Herminghuysen, S. White, A. Kauffman, J. Sanders, S. Li, and L. Cao. "Determination of molten salt mass using ^{22}Na tracer mixed with ^{154}Eu and ^{137}Cs." *Journal of Radioanalytical and Nuclear Chemistry*, Published online: 03 July (2018): 1-7
- L. Cao, J. Jarrell, S. White, K. Herminghuysen, A. Kauffman, D. E. Hardtmayer, J. Sanders, and S. Li. "A radioactive tracer dilution method to determine the mass of molten salt." *Journal of Radioanalytical and Nuclear Chemistry 314, no. 1 (2017): 387-393*

Conference Presentations

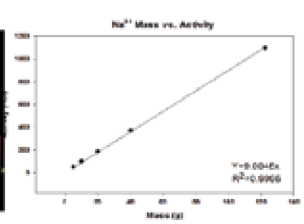
- L. Cao et al, presentation to the 9th International Conference on Isotope, Doha, Qatar, November 12th-16th, 2017
- L. Cao et al, presentation to 11th Methods and Applications of Radioanalytical Chemistry (MARC XI), Hawaii, April 8-13, 2018
- L. Cao at el, presentation to 2018 International Pyroprocessing Research Conference/IPRC, Japan, October 24th-26th, 2018 (submitted)

University Collaborations

- Douglas Hardmayer, supported by the LDRD project, graduated with an M.S. degree in Nuclear Engineering from the OSU in 2018. His thesis title is "A radioactive Tracer Dilution Method for mass determination in LiCl-KCl radioactive Eutectic Salts
- Professor Lei R. Cao, of the Ohio State University has made significant contributions to the proof of concept measurement results



Gamma spectrum of salt sample LiCl-KCl with additional of Na^{22}, Eu^{154}, and Cs^{137}



Radioactivity versus salt mass from measurement of Na^{22} emission from salt with presence of Cs^{137} and Eu^{154}

PROJECT ID: 16-133

INL Initiative: Critical Infrastructure Protection

Secure Supervisory Control and Data Acquisition Communications System

Many digital systems are vulnerable to devastating cyberattacks, and technology to protect these systems is less developed than the capabilities of those seeking to destroy them. The objective of this work was to significantly enhance the cybersecurity of industrial control systems by developing a communication system that includes enhanced situational awareness and leverages unique aspects of control-system networks to make them more immune to attack. This research leveraged new technologies, including software-defined networking, to develop a networking infrastructure that includes unique filtering methods and monitoring capability to allow the operator to understand what is happening and to prevent unwanted actions. The unique aspects of this research include real-time application-level communications monitoring, packet filtering at the application function level, logical network segmentation, and real-time access management. This project may lead to future work with the California Energy Commission Electric Program Investment Charge and the Pale Horse Project.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Briam Johnson

INTERNAL COLLABORATORS (Idaho National Laboratory): Michael McCarty, Rishi Chatterjee

PATENTS:

First filing: A provisional patent entitled "Smart Network Switching Systems and Related Methods," filed June 18, 2018, application number 62/686,300.

NUMBER OF INVENTION DISCLOSURE REPORTS: 1

Idaho National Laboratory

Secure Control Systems Communications System

The goal of this research is to deliver a transformational solution to significantly enhance the cybersecurity of control systems across critical infrastructures through innovations that provide enhanced control and visibility of system processes and data flows.

Problem Statement

- Control system devices are vulnerable to cyber attack. Consequences of a successful attack can be catastrophic to critical infrastructures.
- Security technologies have not kept up with the capabilities of attackers.
- There are no good tools designed for situational awareness of control system network traffic
- Most existing security technologies intended to help make control systems more secure are "bolt-on" solutions that assume that the communications system and endpoints are secure. This is not necessarily the case.

Proposed Solution

Create a new system including the network infrastructure and a network system interface to allow the system operator to monitor and control network flows.

The system leverages unique aspects of control systems, including:

- Predictable network messaging
- Limited numbers of standard protocols (in most cases)
- Relatively static endpoints

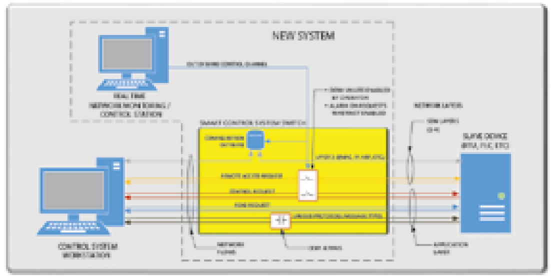
Features & Benefits

- Securely controls network flows by leveraging software defined networking equipment that uses open (but customized) software.
- Assumes that endpoints are not secure/cannot be trusted.
- Provides enhanced situational awareness by allowing the operator to monitor network flows and set alarm limits for abnormal behavior.
- Allows the system operator to adaptively control network flows, including offering a "panic button" to eliminate remote access/control in the case of a cyberattack.

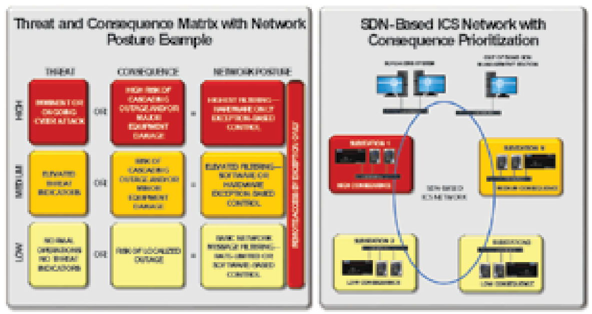
Presentations and Potential Follow-on Work

- Presented to:
  - DOE-OE CYOTE Program Manager
  - DOE-IN Pale Horse Program Manager
  - VADM Jan Tighe/Navy technical working group
- Potential Follow-on work:
  - California Energy Commission EPIC Program (partnering with Southern Cal Edison)
  - Pale Horse Project

Functional Block Diagram



Network Posturing and Prioritization



IDR and Patent Information

- Provisional Patent filed June 18, 2018, serial number 62/686,300
- IDR 4442, docket BA-996 submitted 1/10/2018

INL LDRD: 16-133

INL BUSINESS SENSITIVE INFORMATION

Brian Johnson, Michael McCarty, Rishi Chatterjee

Projects featured in this report resulted in

38 peer reviewed publications

PROJECT ID: 16-152

INL Initiative: Critical Infrastructure Protection

Wireless Radio Frequency Signal Identification and Protocol Reverse Engineering (WiFIRE)

The wireless technology industry is undergoing phenomenal growth in the deployment of networks, applications, and devices. Wireless-industry growth and mandated spectrum sharing increases the exposure of communications infrastructure to malicious actors and interference, which impacts the reliability of communications. Actively and continuously monitoring wireless communications across a broad range of frequencies is the only way an organization knows what wireless activities are taking place in their environment. The objective of this project was to build a wireless radio-frequency signal identification and protocol reverse engineering toolset, usable in an operational context for automatically analyzing the radio-frequency signals and wireless protocols, either in the environment or from a black-box device, and to perform automated wireless-protocol reverse engineering. Wireless radio-frequency signal identification and protocol reverse engineering will enable the government to identify wireless protocols in use, assess the robustness of wireless implementations, analyze traffic, identify potential data leakage, and compare the implementation of a protocol with its official specifications. The novelty of wireless radio-frequency signal identification and protocol reverse engineering is its real-time capability to capture radio-frequency data, quickly identify the protocols in use, and perform protocol reverse engineering.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Kurt Derr

INTERNAL COLLABORATOR (Idaho National Laboratory): Samuel Ramirez

PATENTS:

First filing: Provisional Patent application entitled "Spectrum Monitoring and Analysis and Related Methods, Systems, and Devices," filed 5/18/18, application number 62/673/545; BA-961P2.

Wireless Radio Frequency Signal Identification and Protocol Reverse Engineering (WiFIRE)

Dr. Kurt Derr and Sam Ramirez

National Challenge: Unique *real-time* wireless signal detection and classification for government, commercial, and university use

IMPACT

Quickly identify and characterize spectrum sources to identify wireless signals and protocols.

- To protect critical infrastructure communications
- To enable telecommunication; provide and manage spectrum access

BACKGROUND

Wireless technology is undergoing phenomenal growth.

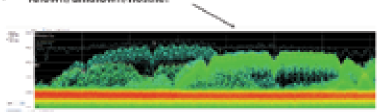
- 10% annual growth rate for WiFi (WiFi Alliance, Jan 2015)
- 99% of Americans have access to cellular networks

New systems will use spectrum observation and sharing mandated by government.

- Makes it harder to detect transmissions hostile to critical infrastructure
- National effort under way to document spectrum use

PROBLEM

- What are these wireless signals?
- Known/unknown/hostile?



COLLABORATORS

University of Utah:

- Professors: Dr. Sneha Kasera
- Ph.D. Students: Christopher Becker, Aniqua Baset

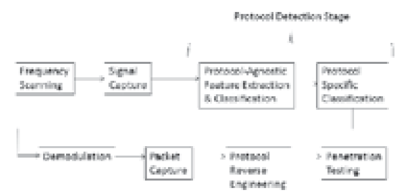
INL LDRD 16-152
INL/MIS-16-38971

APPROACH

- Utilize software defined radio to monitor a broad swath of wireless spectrum
- Utilize GNU Radio framework and develop custom signal processing blocks as needed for real-time performance
- Develop novel classification techniques based on machine learning and pattern matching for a variety of wireless signals (e.g., WiFi, Bluetooth, Zigbee, 802.11p, unknown signals)
- Develop/build auto-tunable classification system that can automatically adjust to different computational and RF environments

SOFTWARE DEFINED RADIO

DESIGN PROCESS FLOW



- Scan wireless spectrum and capture signal using software defined radio
- Extract signal features by frequency, timing, or phase analysis
- Determine the protocol using machine learning techniques
- Demodulate the signal and capture packets
- Optionally reverse engineer the protocol and conduct penetration testing

RESEARCH OBJECTIVES

Wireless

- Perform real-time identification and classification of wireless signals over the air or from physical black box
- Blind identification and decoding of signals and protocols
- Identify wireless interference issues
- Infer or validate wireless signal protocol implementations
- Contribute to national spectrum measurement observations and database

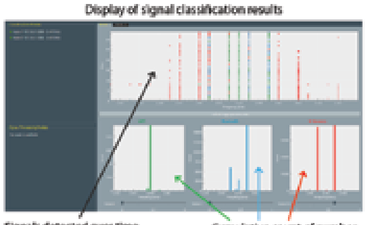
Cyber

- Reverse engineer protocols
- Uncover potential vulnerabilities with penetration testing
- Understand how an adversary would gain control of device
- Mitigate and shore up vulnerabilities

RESULTS

- Working prototype developed that is scalable to both N classification and signal processing nodes
- Able to identify multiple WiFi, ZigBee, and Bluetooth signals in test area simultaneously
- Low number of false identifications
- Blind-signal analysis in progress

Display of signal classification results



Signals detected over time WiFi → green; Bluetooth → blue; Unknown → red

Cumulative count of number of detections of specific frequencies

PROJECT ID: 17A1-079

INL Initiative: Critical Infrastructure Protection

Affixing Inert Dissimilar Materials to Structural Materials for High Performance Armor Systems

High-performance armor systems will require sector–disrupting performance improvements that can resist advanced threats while maintaining a low areal density for fuel savings and vehicle agility. These requirements can potentially be met if extremely hard ceramic materials can be metallurgically affixed to metallic structural materials, resulting in significant reductions in the weight of the armor system and increasing overall structural flexural stiffness. Various processes, such as encapsulation with metal alloy and three dimensional front-to-back through-thickness reinforcement, have been attempted to affix or bind ceramics to structures. These processes have shown improved ballistic performance, but the fabrication process is labor intensive and neither economically viable nor conducive to integration into vehicular structural components. The goal of this project was to metallurgically affix ceramic tile to structural alloys to simplify fabrication of economical, high-performance armor systems integrated into structural components. The approach was successfully demonstrated to yield significantly lower areal density systems that efficiently defeat various high-level ballistic threats. The results of this project contributed to less loading on armored vehicles and personal protective vests through effective integration of advanced lightweight armor materials with conventional metal armor and structural materials. The results have been communicated to various military stakeholders who have expressed interest in follow-on development.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Thomas Lillo

INTERNAL COLLABORATORS (Idaho National Laboratory): Joshua Kane, Adrian Wagner, Henry Chu

Idaho National Laboratory

Affixing Inert Dissimilar Materials to Structural Materials for High Performance Armor Systems

PI -T. Lillo Co-investigators -J. Kane, A. Wagner Technical Monitor -H. Chu

Objective

Develop innovative methods that metallurgically affix ceramics to metals to enable economically efficient design and production of light armor systems that survive ballistic and blast threats.

Approach

a) Conduct proof-of-principle study demonstrating effective bonding of SiC armor to steel and titanium armor plates
b) Characterize the bonding materials' structural and performance properties
c) Optimize affixing methods to enable future research in bonding of a broad range of ceramics (super hard, incompressible B_6O; WB_4) to structural alloys.

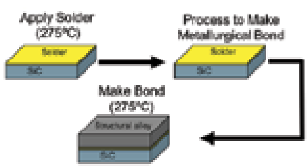
Impact

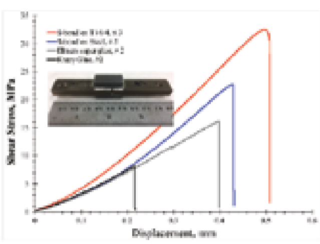
"Lighten the load" of armored vehicles and personnel protection vests through effective integration of advanced lightweight armor materials with conventional metal armor and structural materials.

Technical Challenges:

- Low reactivity (inert) nature of SiC
- Coefficient of thermal expansion mismatch between SiC and metal alloys

Option 1 –Solder Approach



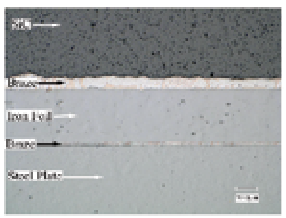


Notable Results:

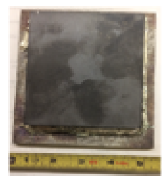
- **Bond Shear strength: SiC/Armor Steel: 23 MPa**
  (>50% increase over organic adhesive)
- **Bond shear strength: SiC/Ti-6Al-4V: 32 MPa**
  (>100% increase over organic adhesive)

Option 2 –Brazing Approach (Higher bond strength)

Multi-layer Approach (CTE mismatch mitigation)

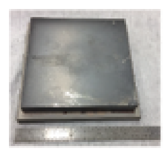


Examples of Bonded Targets



SiC soldered to Ti-6Al-4V

SiC soldered to Steel



SiC brazed to Steel

Ballistic Testing (scheduled for Sept. 6 & 7, 2018)

Test Threat: 7.62 x 51 mm M993 WC core

SiC/Ti-6Al-4V Systems

Thickness Ti-6-4	Thickness SiC	Areal Density, lbs/ft^2	Ratio Ti:SiC	Total thickness, inch
0.1875	0.25	8.46	1.33	0.4375
0.2	0.225	8.33	1.13	0.425
0.1875	0.225	8.05	1.20	0.4125
0.225	0.15	7.65	0.67	0.375
0.17	0.225	7.65	1.32	0.395
0.1875	0.2	7.68	1.07	0.3875
0.125	0.25	7.08	2.00	0.375

SiC/Steel Systems

Thickness Steel	Thickness SiC	Areal Density, lbs/ft^2	Ratio Steel:SiC	Total thickness, inch
0.145	0.25	10.09	1.72	0.395
0.155	0.225	10.08	1.45	0.38
0.13	0.25	9.48	1.92	0.38
0.14	0.225	9.47	1.61	0.365
0.17	0.15	9.44	0.88	0.32
0.115	0.225	8.45	1.96	0.34
0.125	0.2	8.44	1.60	0.325

Test Threat: 0.50 cal AP

SiC/Steel Systems

Thickness Steel	Thickness SiC	Areal Density, lbs/ft^2	Ratio Steel:SiC	Total thickness, inch
0.365	0.5	23.23	1.37	0.865
0.34	0.5	22.21	1.47	0.84
0.225	0.5	17.52	2.22	0.725
0.2	0.5	16.30	2.50	0.7
0.1875	0.5	15.98	2.67	0.6875

SiC/Ti-6Al-4V Systems

Thickness Ti-6-4	Thickness SiC	Areal Density, lbs/ft^2	Ratio Ti:SiC	Total thickness, inch
0.41	0.5	17.73	1.22	0.91
0.222	0.5	13.43	2.25	0.722

Work supported through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

LDRD: 17A1-079 INL/MIS-18-51070

PROJECT ID: 17A1-156

INL Initiative: Critical Infrastructure Protection

Nuclear Safety Systems Cybersecurity

Safety systems are dependent upon heavily in nuclear plants, oil and gas manufacturing, and other critical infrastructure sites. Safety systems are designed and tested to ensure plant safety, prevent accidents, and reduce damage and harm if an accident occurs. In the past, these systems—in the nuclear sector—have been deployed as analog systems with no digital controls or devices. As these analog safety systems age, replacement parts become extinct, and repairing the components has become the only option for keeping these systems alive. An alternative solution that has already been embraced by other industries relies on digital safety systems and triple modular redundancies; however, these systems have not yet faced the scrutiny of cybersecurity. The inherent trust the nation places on safety systems must be validated and corroborated.

The goal of this work was to investigate the security of core control protocols and architectures used in the subsystems of a typical nuclear power plant's safety system. Research was limited to a select set of critical components to evaluate the cyber strengths and weaknesses of the controlling protocols and to develop concepts for strengthening the cybersecurity features of these components. This research is directly applicable to characterizing future cyber-research and engineering designs that can enhance the security of safety systems within a nuclear facility. This work has led to possible collaborations with research agencies, including the Korean Atomic Energy Research Institute and the United Arab Emirates.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Jonathan Chugg

INTERNAL COLLABORATOR (Idaho National Laboratory): Kenneth Rohde

Award Winner: Third Place in INL Poster Competition

Idaho National Laboratory

Nuclear Safety Systems Cybersecurity

17A1-156FP

Jonathan Chugg

National Challenge: Ensure the cybersecurity of nuclear facility safety systems

Impact

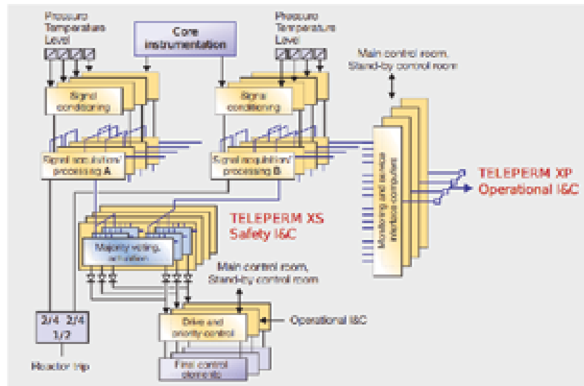
- This research will provide a scientific-basis for cyber-informed engineering of future nuclear safety system designs
- Experimental results will influence the research priorities for nuclear-cybersecurity research programs.

Background

- Safety systems are critical features in protecting the public.
- Safety systems are designed and tested to ensure public safety, maximize plant safety, and prevent accidents if an unsafe state occurs.
- Nuclear sector safety systems have traditionally been analog with no digital controls.
  - These analog safety systems are aging and replacement parts are becoming extinct.
  - The alternative digital safety system solutions are being embraced by international nuclear sites.
- New and increasing risks need to be analyzed and mitigated if/when our nation's and international nuclear infrastructure migrate to digital safety systems.

Approach

- Investigate the security of the core control protocols and architectures used in the subsystems of a typical nuclear power plant's safety system.
- Select a limited set of critical components to evaluate the cyber strengths and weaknesses of the control protocols
- Develop concepts for strengthening the cybersecurity features of these components.
- Conduct peer-reviews with vendors and asset owners to optimize research pathways for mitigations
- Increase the confidence level of critical safety system components and design
- Collaborators: Boise State University, Purdue University, Private Company



Digital safety systems in the nuclear sector are starting to be embraced, such as the Areva TELEPERM XS system used in a few U.S. nuclear power plants.

Research Opportunities

- Potential research of international deployment of APR-1400
- Optimize application of results across nuclear monitoring, security, safeguard, emergency response, and balance of plant systems
- Enhance threat analyses and mitigation solution options for future Consequence-driven Cyber-informed Engineering analyses

BOISE STATE UNIVERSITY

PURDUE UNIVERSITY

PROJECT ID: 17A1-160

INL Initiative: Critical Infrastructure Protection

Mass Storage Equipment Protection

Protecting mass storage devices that contain sensitive and classified information is critical as they contain materials that must be protected during an evacuation or theft scenario. The goal of this project was to enable a faster method for mass storage protection than is currently used in many overseas embassies. Current technology for destruction of magnetic and/or solid-state hard drives involves a mechanical shredder. This shredder can effectively destroy a hard drive, but it often can take minutes to destroy each drive, which can endanger personnel under attack and requires electrical power that may be interrupted at critical times. Thermite-torch technologies could be employed to destroy multiple hard drives at once in a fraction of a second, thus protecting sensitive material while minimizing time and power-load requirements for destruction of the drives. Testing showed that several layers of each substrate material could be destroyed by a thermite torch. When the thermite formulation was modified, the destruction level to the different substrate materials varied. Using these data, optimal torch formulas can be estimated for multiple devices based on the materials of their construction. The thermite torch completely destroyed the area it targeted, leaving no data behind. The project built upon previous experience with thermite-torch technologies, testing various devices to determine penetration power and coverage against different mass storage devices. Project researchers are exploring funding opportunities through various government agencies for possible applications in overseas areas.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Nikki Rasmussen

INTERNAL COLLABORATORS (Idaho National Laboratory): Steven D'Arche, James Schondel

Idaho National Laboratory

Mass Storage Equipment Protection

Nikki Rasmussen (PI), Steven P. D'Arche

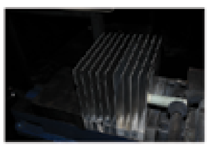
LDRD: 17A1-160
INL/EXT-18-50292

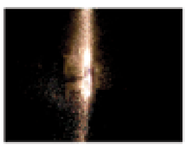
Proof-of-Principle: Rapid, safe, effective, and efficient destruction of data for a broad range of data devices and systems

Impact: Protect national security by preventing the loss of sensitive information through quick and reliable total destruction of digital storage devices in 'loss of control' events.

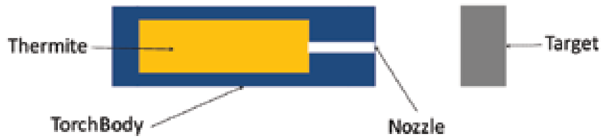
Types of Digital Storage Devices

Tailorable Size and Damage





Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517



Approach:

a) Develop thermite torches using different design parameters (i.e., formulation, shape, nozzle, etc.)
b) Characterize thermite torch design parameters against typical digital storage materials of construction (e.g., aluminum, circuit boards, glass, silicon chip, etc.)
c) Optimize system performance to achieve 'forensically unrecoverable' destruction of data

BEA's Recently Awarded Energetic Materials Patents:

- **US Patent number 9,481,614** - Energetic Materials and Methods of Tailoring Electrostatic Discharge Sensitivity of Energetic Materials
- **US Patent number 9,488,452** - Apparatus for rendering at least a portion of a device inoperable and related methods
- **US Patent number 9,908,823** - Flexible Energetic Materials and Related Methods
- **US Patent number 9,939,235** - Initiation Devices, Initiation Systems including Initiation Devices and Related Methods
- **US Patent number 10,042,397** – Energetic Potting Materials, Electronic Devices Potted with the Energetic Potting Materials, and Related Methods

PROJECT ID: 17A1-162

INL Initiative: Critical Infrastructure Protection

Securing Electronic Control Unit Communication

Researchers have shown that controller-area-network (CAN) bus systems in the automotive industry lack necessary security features. Public and industry research and development has only focused on CAN bus security through third-party add-ons, which provide only a quick-fix approach to this national grand challenge. Electronic control units (ECUs) are designed to meet original equipment-manufacturers' (OEMs') parameters for functionality whereas the actual coding structure used within the ECU is a black box to OEMs and Tier 1 suppliers, making them very difficult to secure using traditional methods. This project investigated the possibility of "injecting" host-based security directly into ECU firmware on a binary level, thus securing ECUs through binary code injection. Researchers were able to develop a proof of concept binary injection in an ECU, modifying the communication protocols with a Diffie-Hellman cryptographic key exchange to secure communications. The John A. Volpe Center of the Department of Transportation and various Department of Defense agencies have expressed interest in this technology.

PRINCIPAL INVESTIGATOR (Idaho National Laboratory): Jonathan Chugg

INTERNAL COLLABORATORS (Idaho National Laboratory): Carl Hurd, Stephen Kleinheider, Matt Wiseman, Kenneth Rohde

INTERNAL COLLABORATOR (Idaho National Laboratory and New Mexico Tech): Sean Salinas

Idaho National Laboratory

Cybersecurity of Building Systems

Access, Management, & Automation

17A1-152FP
Jonathan Chugg
Samuel Ramirez, Edward Springer, Derek Smith, Kenneth Rohde

National Challenge: Cyber protect the access, management, and automation systems used within public and private facilities

Impact

- This research will provide a scientific-basis for cyber-informed engineering that enhances the reliability and resilience of interconnected building management systems
- Experimental results will influence research priorities for access control and automated building and energy management control systems

Background

- Building systems are widely used in a number of different critical infrastructure sectors (e.g. nuclear facilities, power generation facilities, manufacturing facilities, federal facilities)
- These more interconnected systems create new and increasing risks to our nation's infrastructure and economic security
- Connectivity of these building systems are becoming commonplace
- Automated buildings will have connectivity to the Smart Grid, a potential external pathway

Approach

- Fuse cyber and engineering design to create synergistic 'cyngineering' and build a culture of cyber-informed engineering
  - Explore potential possibilities of bypassing, over-taking, and exploiting each system
  - Identify vulnerabilities and proper mitigations and increase confidence level
  - Conduct peer-reviews with vendors to assess mitigation options and design methodologies to create a culture of cyber-informed engineering

Research Progress

- Analysis of Pro 3200 series access control system, extracted firmware, reverse engineered to detect vulnerabilities, discovery of vulnerabilities and proposed mitigations
- Cooperative agreement with Honeywell, providing state of the art technology for building automation systems

Idaho National Laboratory