Pacific Northwest NATIONAL LABORATORY

Nuclear Process Science Initiative NEWSLETTER

The Nuclear Process Science Initiative (NPSI) is a Pacific Northwest National Laboratory (PNNL) internally-funded effort to advance nuclear process science capabilities to meet national needs in environmental management, nonproliferation, and other areas. The five-year initiative was launched in mid-2015.

***NPSI's vision** is to understand, harness, and exploit interfacial phenomena controlling the behavior of materials in nuclear processing.*

Researchers are working in three "thrust" areas:

***Science Thrust 1**:*
Legacy Waste

***Science Thrust 2**:*
Nuclear Security

***Science Thrust 3**:*
Analytical Capabilities

NPSI Leadership:
Initiative Lead: Reid Peterson
Deputy Lead: Brienne Seiner
Thrust 1 Lead: Reid Peterson
Thrust 2 Lead: Jon Schwantes
Thrust 3 Lead: Kevin Rosso
Project Coordinator: Barb Beller
Finance: Debbie Lucas

September 2019

Reid's Notes

Taking the Initiative Leads to Results

By Reid Peterson, Initiative Lead

It doesn't seem that long ago we started talking about the need for a nuclear process science-focused research effort, and then went through the Laboratory's rigorous deep dive process, eventually gaining approval to stand up this initiative.

But here we are, about five years later, and less than one year from completing NPSI. The weeks and months have passed quickly, and I'm pleased that the entire NPSI team has maintained a focus on "time is of the essence" in initiating and completing projects.

Our researchers have contributed new findings to the body of scientific knowledge, developed new research methods, and offered concepts that could change, for example, how waste is processed at Hanford. We've also, importantly, helped strengthen capabilities at the Radiochemical Processing Laboratory. As I look back over our work to date, I couldn't be more proud.

Communications: Tim Ledbetter

Visit the NPSI Website
Contact Us

Wang Presents at International Gathering

NPSI's Zheming Wang was the first speaker when the 2019 MIGRATION conference got underway in Kyoto, Japan, last week.

He presented his NPSI project team's work on, "Metal Ion Sorption on Aluminum Oxyhydroxides under Conditions of High Level Waste Tanks - A Sum Frequency Generation-Vibrational Spectroscopy Study."

MIGRATION conferences provide an international forum for the timely exchange of scientific information on chemical processes controlling the migration behavior of actinides and fission products in natural aquifer systems.

Research Spotlight

For me, a particular source of satisfaction is our progress in journal publications. In this edition of the newsletter, you'll read about recent placements in the *Proceedings of the National Academy of Sciences* and *Scientific Reports*. We've had a number of papers published and accepted for publication, and others still have been submitted for consideration--or will be soon.

Publication of papers in impactful journals is key to building awareness of our staff and capabilities, and really underscores the value that Laboratory Directed Research and Development initiatives can bring to PNNL's science and technology enterprise.

Reid

Two Perspectives

Advisory Committee Chair, CSTO Discuss NPSI Progress

Karthik Subramanian*, Chief Engineer at Washington River Protection Solutions, has served as NPSI Advisory Committee chair since the initiative's start.* ***Sue Clark*** *led NPSI for its first couple years before she was named the PNNL Energy and Environment Directorate (EED) Chief Science and Technology Officer (CSTO) in 2017. With NPSI set to largely close out in the spring-summer 2020 timeframe, we talked with Subramanian and Clark about some of their impressions of NPSI accomplishments.*

How effective has NPSI been in achieving staff development goals?

Subramanian: When I first heard about NPSI, one of the major things the initiative wanted to accomplish was to begin training the next

Initiative's Papers Appear in Prominent Journals

A Window into the Hidden Nuclear World

A team of researchers from NPSI, Lawrence Berkeley National Laboratory, and the University of Chicago has developed a first-of-its-kind imaging approach to directly map the chemistry of actinides at the atomic level. The method uncovered unique behavior that will help scientists improve the safety and performance of nuclear fuels.

As reported in the *Proceedings of the National Academy of Sciences*, the team examined the surface of uranium dioxide (UO2) single crystals. When these crystals are exposed to air for extended periods, defects can form that degrade the integrity of the material. To date, most of the research on this system has been performed using X-ray techniques, which, while powerful, are limited in their ability to directly detect changes in the material's structure and chemistry.

Using an advanced scanning transmission electron microscope recently launched in PNNL's Radiochemical Processing Laboratory, the team looked at and imaged both pristine and aged UO2 surfaces, revealing clear changes in just the top few nanometers of the material caused by air exposure.

The team used the microscope's state-of-the-art electron energy loss spectrometer to acquire atomic-level chemical maps of uranium and probe the nanoscale oxygen

generation of staff, and also finding meaningful work for those folks so they can have a career in nuclear process science. I think realization of that goal is probably the initiative's major accomplishment. It will be a huge success story if NPSI and PNNL can continue the progress, and keep these staff employed and engaged in the work.

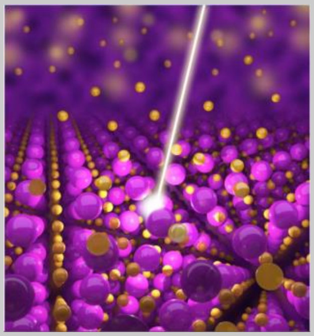
Clark: NPSI has been quite transformational in this regard. Laboratory Directed Research and Development funding, which supports NPSI, is a way we help manage our human capital pipeline in EED and PNNL. The initiative very successfully transitioned and created new opportunities for staff, bringing in postdocs, graduate students, and undergraduates, but then also transitioning staff that already were in those types of temporary positions to early-career roles as Scientist & Engineer levels 2, 3, and 4.

How influential has NPSI been in strengthening the Radiochemical Processing Laboratory (RPL), which was a key objective of the initiative?

Subramanian: NPSI has had a huge influence on RPL's renaissance. What the initiative has accomplished in getting attention for RPL, getting programs and projects for RPL--you take a step back and look at that from a very high level and it's really an impressive success story. From my personal standpoint related to tank farm processing, I believe RPL is going to be absolutely necessary for future work at Hanford to be successful.

Clark: When PNNL decided to keep the RPL, it took NPSI investments, General Research Equipment funding, and facility modification to build out our capabilities in that building, which is helping us evolve existing programs and create and obtain new ones. RPL still is a very expensive facility to operate, but you can do such unique things out there, and we have learned that sponsors, if they need the kind of environment in the material. This result is the first such atomic-scale analysis of any actinide material.

For more information on the research approach and additional findings, see this PNNL research highlight.



PNNL graphic designer Mike Perkins created this illustration of atomic-scale imaging of the UO2 crystal surface in the transmission electron microscope.

Project Offers Revelations on Tough Materials

A NPSI research team has identified reasons why certain materials may be able to survive rough-and-tumble environments and still maintain their functionality. The findings could be key to making more reliable space-based electronics, nuclear power plant sensors, and nuclear waste forms.

The team's research focused on understanding the evolution of oxide pyrochlore materials in extreme radiation environments. Pyrochlores have long been studied for radiation-related applications, but it has not been clear how the

work done in that type of facility, they're absolutely willing to pay for the costs of doing the work at RPL. So NPSI's contributions to strengthening RPL have been significant.

What else stands out to you about NPSI progress and accomplishments?

Subramanian: When you take a step back and look at NPSI, it's a success. In this business, people have 10-, 15-, and 20-year outlooks. What NPSI has been able to accomplish in a relatively short amount of time, 3 to 4 years to date and with about $15 million in funding (when it ends next year), it has been impressive. And then you consider what the NPSI team has achieved in getting attention for RPL, adding programs and projects there--it's a great accomplishment, and I'm excited to see what happens in the final year. Personally, my participation as committee chair has been very enriching. I have learned a lot from PNNL and NPSI leadership, regarding their own programs and how to develop activities like an initiative from an internal commitment. Working with the other advisory committee members also has been great--they're really top-notch folks.

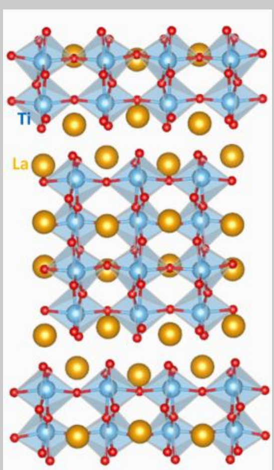
Clark: One accomplishment is advancement of the task-specific release plan process, which was championed by NPSI. This approach allows PNNL to work with radioactive materials in the hazard facility of RPL, and work in a way that manages the risk and minimizes the size of the sample. Researchers can then take these tiny samples out of the RPL and safely access and use other capabilities at PNNL, whether it's the Environmental Molecular Sciences Laboratory or other facilities. The process also enables access to unique facilities not on the PNNL campus--such as light sources, x-ray synchrotron light sources, and neutron sources within the U.S., and even around the world. That process has been very important in terms of building capabilities.

material's basic framework, the crystal lattice, responds to ionizing radiations.

The team investigated the material's behavior using advanced computer simulations that allowed the researchers to access fast structural distortions at the atomic level that can't be measured with high accuracy in laboratory experiments. The study revealed how the crystal lattice deforms under irradiation, eventually leading to complete loss of order through a process called amorphization.

A paper chronicling the results was published in *Scientific Reports.*

For more information on the research approach and findings, see this PNNL research highlight.



Molecular dynamic simulations of a layered perovskite oxide material show how the lattice distorts under ionizing radiations.

NPSI Annual Review Outcomes Include Focus on Future

NPSI received solid marks during its final Annual Review, July 9-10 at PNNL.

The initiative's advisory committee, made up of PNNL and external experts, concluded that NPSI:

- Created state-of-the-art techniques and re-established a "center of excellence" quality in nuclear process science at PNNL and the Radiochemical Processing Laboratory
- Established a pipeline of staff to support nuclear process science
- Developed necessary processes to efficiently work with radioactive materials
- Was highly successful in terms of initial goals and the ability to pivot in a highly dynamic customer environment.

Advisory committee members challenged the initiative's leadership team to ensure NPSI-developed practices continue to strengthen PNNL's nuclear science research.

The committee also recommended that NPSI maintain focus on delivering groundbreaking journal papers and continue to promote, at a PNNL institutional level, methods that foster cross-directorate collaboration.

NPSI will start ramping down later this fall, with all projects set for completion in the spring-summer 2020 timeframe.

NPSI Publications

March - September 2019

Note: Some links may work only for PNNL staff.

Journal Articles:

Spurgeon, S., M. Sassi, C. Ophus, J. Stubbs, E. Ilton, E.Buck. 2019. "**Nanoscale Oxygen Defect Gradients in UO2+*x* Surfaces**," *Proceedings of the National Academy of Sciences*. 116(35) 17181-17186. DOI: 10.1073/pnas.1905056116.

Asmussen, S.E., A.M. Lines, D. Bottenus, F. Heller, S.A. Bryan, C. Delegard, C. Louie, G. Lumetta, K. Pellegrini, K.W. Pitts, S. Clark, A. Casella. 2019. "**In situ Monitoring and Kinetic Analysis of the Extraction of Nitric Acid by Tributyl Phosphate in N-Dodecane Using Raman Spectroscopy**," *Solvent Extraction and Ion Exchange*. 37(2) 157-172. DOI: 10.1080/07366299.2019.1630071.

Kerisit, S.N., Z. Shen, M.P. Prange, E.S. Ilton. 2019. "**Separation of Radiolytic Species at the Boehmite-Water Interface**," *Journal of Physical Chemistry C*. 123(25):15534-15539. DOI: 10.1021/acs.jpcc.9b02144.

Sassi, M. T.C. Kaspar, V. Shutthanandan, K.M. Rosso, S.R. Spurgeon. 2019. "**Effect of Structure and Composition on the Electronic Excitation-induced Amorphization of La2Ti2-xZrxO7 Ceramics**," *Scientific Reports*. DOI: 10.1038/s41598-019-44621-5.

Fetisov, E., W. C. Isley, G.J. Lumetta, S.M. Kathmann. 2019. "**Electric Potentials of Metastable Salt Clusters**,"*Journal of Physical Chemistry C*. DOI: 10.1021/acs.jpcc.9b02494.

NPSI held its final Annual Review in July in PNNL's Systems Engineering Building. The initiative received strong endorsement from its advisory committee for accomplishments of the past year, as well as previous years.

Thrust 2 Projects Contribute Insights into Crud Formation, Chemical Fractionation, and Noble Metals

A number of NPSI projects concluded in fiscal year (FY) 2018 and early FY 2019. In past editions, the NPSI Newsletter has reviewed outcomes of completed or concluded projects. The three projects featured below are associated with Science Thrust 2 (Nuclear Security). Additional projects that have been completed will be highlighted in the next edition.

Project: Interfacial Diffusion and Crud Formation at the Liquid-Liquid Interface of Solvent Extraction Processes
Principal Investigator: Amanda Casella
Outcomes: The project targeted a fundamental understanding of how crud (solids) forms at the liquid-liquid interface during solvent extraction processes. Initially, the project examined

Palmer, C., K. Gerez, J.M. Schwantes, R.A. Clark. 2019. "**Scoping Evaluation of Trace Isotopic Ratios within the Noble Metal-phase**," *Progress in Nuclear Energy*. 117:103059. DOI: 10.1016/j.pnucene.2019.103059

Lach, T.G., D.J. Edwards, E.C. Buck, B.K. McNamara, J.M. Schwantes, R.A. Clark. 2019. "**Fission Recoil-induced Microstructural Evolution of the Fuel-cladding Interface (FCI) in High Burnup BWR Fuel**," *Journal of Nuclear Material*. 521:120-125. DOI: 10.1016/j.jnucmat.2019.04.044.

Pellegrini, K.L., C.Z. Soderquist, S.D. Shen, E.J Krogstad, C.J. Palmer, K.Z. Gerez, E.C. Buck, T.G. Lach, J.M. Schwantes, R.A. Clark. 2019. "**Chemical and Isotopic Characterization of Noble Metal Phase from Commercial UO2 Fuel**," *Analytical Chemistry*. DOI: 10.1021/acs.analchem.8b05549.

Rovira, A.M., J. Geeting, R.A. Peterson, J.R. Allred, R.W. Shimskey, C. Burns, K.A. Colosi. 2019. "**Media Comparison of Filtration with Hanford Tank AP-107 Supernate**," *Separation Science and Technology.* 54(12): 1912-1921. DOI:10.1080/01496395.2019.1575419.

Bair, J.L., D.G. Abrecht, D.D. Reilly, M.T. Athon, J.F. Corbey. 2019. "**Phase Field Model of Uranium Carbide Solidification Through a Combined KKS and Orientation Field Approach**," *Journal of Physics Condensed Matter*. 31(12): 125901 DOI: 10.1088/1361-648X/aafd69.

New Brochure Highlights Staff, Research, and More

historical Hanford Site records, along with other open-literature published work to provide the framework and prioritization for experiments. The next step involved establishing and validating macro-scale testing along with implementation of complementary microfluidic studies--both aspects used in situ monitoring by Raman spectroscopy. In addition to experiments, computational approaches, including fluid dynamic modeling, were employed to gain further molecular insights regarding liquid-liquid interfacial processes. In the project's final year, systems involving mixtures of degradation products with the typical extraction components were studied to determine complexation and effects. Crud formation was studied within a microfluidic device to give a better understanding of fundamental rates of transfer, drivers, nucleation, and complexation at the liquid-liquid interface. The project provided stronger, more holistic fundamental understanding of crud formation.

Project: Monitoring Diffusion of Actinide Daughters and Granddaughters in Metals for Chronometer Applications
Principal Investigator: Dallas Reilly
Outcomes: This project focused on understanding trace element fractionation during the production, casting, or melting of uranium (U) metal or other actinide metals. The research effort combined high-temperature controlled experiments, molecular-scale observations, and theoretical modeling. One experiment showed, for the first time, quantitative fractionation of thorium (Th) during the production of U metal (in a conversion to uranium tetrafluoride to the metallic phase in a process known as bomb reduction). In that study, Th moved from the tetrafluoride to the crucible and slag during the reduction. Modeling experiments focused on carbon in the U metal system, since the resulting U carbides could potentially scavenge trace elements like Th during these reactions. The studies produced a novel way of seeding crystals in phase field models. Finally, in seeking

NPSI has developed a four-page brochure that covers the initiative's projects and progress.

The brochure is for anyone who wants to learn more about NPSI objectives, research contributions, publication statistics, collaborators, and initiative-sponsored events. The two middle pages can be displayed as a poster. The brochure also includes photos and other information that highlight NPSI staff.


NUCLEAR PROCESS SCIENCE INITIATIVE (NPSI)

NPSI is a five-year, multi-million-dollar Pacific Northwest National Laboratory (PNNL) investment focused on building capabilities to:

- Enable resolution of the nation's legacy wastes from decades of weapons production
- Develop new signature discovery approaches for nuclear forensics and nonproliferation.

Since it began in 2015, NPSI has been investing in people, programs and capabilities to advance the initiative's research aims and to help establish PNNL's Radiochemical Processing Laboratory (RPL) as a premier national resource for research and development test beds. NPSI's research projects are organized in three "thrust" areas: Legacy Waste, Nuclear Security, and Analytical Capabilities.

NPSI ACCOMPLISHMENTS IN PHOTOS

Researchers developed the world's first liquid cell radAFM capability for studying beta and gamma radiation effects, with a focus on metal-oxide interfaces with aqueous solution.

NPSI's use of the Focused Ion Beam in RPL has helped enable advances in understanding noble metals and more fully using research instrumentation across PNNL.

Raman spectroscopy measurements supported NPSI's efforts to learn more about the formation of interfacial solids that occur during solvent extraction of nuclear fuel.

NPSI researchers developed an X-ray diffraction approach that facilitated quantitative microstructural properties analysis spanning scales.

STAFF FROM ACROSS PNNL HAVE MADE CONTRIBUTIONS TO NPSI

to monitor the fractionation of plutonium (Pu) daughter products during a similar bomb reduction experiment as the U, atom probe tomography (APT) was performed on a bomb-reduced Pu metal. This first-ever Pu APT method resulted in valuable information on the bomb reduction process and corrosion mechanism. The project outcomes will benefit the nuclear forensics community and worker health and safety related to production of metallic nuclear fuels.

Project: Ion Implantation and Characterization of Epsilon Metal Phase Formation in Ceria
Principal Investigator: Ram Devanathan
Outcomes: This project filled key knowledge gaps in noble metal particle formation in irradiated nuclear fuel, which could enhance the safety and economics of nuclear energy. It tackled the challenge of identifying alloy nanoparticle formation mechanisms. The project took a novel approach, combining computer simulations of radiation damage, thermodynamic calculations, and ion bombardment of a surrogate material to enhance understanding of nuclear fuel. Researchers irradiated ceria doped with molybdenum (Mo), ruthenium (Ru), rhodium (Rh), palladium (Pd) and rhenium (Re). The samples were characterized with electron microscopy and elemental mapping from selected areas. Researchers also analyzed the thermodynamic properties of high entropy alloy particles. Significantly, the project found that radiation-enhanced diffusion plays an important role in initial stages of nanoparticle formation and thermal diffusion contributes to alloying and particle coarsening. The researchers further found that MoRuRhPd-based alloys are thermodynamically stable as single-phase solid solutions over a broad composition range. The project established external collaborations for in situ characterization of nanoparticle formation and connected the findings with results of a similar NPSI project on uranium dioxide.

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Nuclear Process Science Initiative
energyenvironment@pnnl.gov

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