The Nuclear Process Science Initiative (NPSI) is a Pacific Northwest National Laboratory 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**:*
Linking Interfacial Phenomena to Bulk Properties

***Science Thrust 2**:*
Interfacial Phenomena Driving Chemical Fractionation

***Science Thrust 3**:*
Radiation at Interfaces.

NPSI Leadership:

Initiative Lead: Sue Clark
Deputy Lead: Matt Douglas
Thrust 1 Lead: Reid Peterson
Thrust 2 Lead: Jon Schwantes

May 2017

Sue's Space

Sue Clark, Initiative Lead

Welcome to the first edition of the Nuclear Process Science Initiative Newsletter. This is one of the ways we'll keep you up-to-date with NPSI progress and accomplishments.

The initiative is advancing on many fronts as we work to leverage fundamental science discoveries to develop capabilities and effective technologies for waste cleanup and nonproliferation purposes.

Here are a few NPSI progress highlights, which we address in more detail elsewhere in the newsletter:

- We're seeing some outstanding findings from our 11 active projects, reflected in a growing number of journal papers.
- One of our project teams has developed a breakthrough sample preparation technique that makes it possible to study used nuclear fuel safely and more cost-effectively.
- Another team established a new process to enable transfer of miniscule radioactive samples across PNNL and off-site, which improves access to top-flight instrumentation for our studies.

Thrust 3 Lead: Kevin Rosso
Project Coordinator: Barb Beller
Finance: Debbie Lucas
Communications: Tim Ledbetter

Visit the NPSI Website

Initiative Thrust Lead Elected AIChE Fellow

Peterson

Reid Peterson, who leads the Nuclear Process Science Initiative's science thrust focused on linking interfacial phenomena to bulk properties, has recently been elected a Fellow of the American Institute of Chemical Engineers (AIChE).
More info...

NPSI Sponsors Alexandra Navrotsky's April 20 Seminar at PNNL

Internationally-recognized scientist **Alexandra Navrotsky** of the University of California-Davis presented the seminar, "Lanthanides and Actinides - Why Thermodynamics Matter," at PNNL on April 20. Approximately 50 PNNL staff attended

- The initiative has hosted leading researchers to speak at PNNL, and our staff organized a symposium at the recent American Chemical Society national meeting.

I could not be more pleased with our progress in changing the paradigm for nuclear materials processing and its signatures. I hope you find this newsletter informative and useful, and I look forward to sharing additional accomplishments in future editions.

Sue

Research Spotlight:

Findings Published in RSC Advances Provide New Insights into Chromium's Impact on Boehmite Reactivity

NPSI research results published in RSC Advances could inform development of more effective methods for addressing boehmite dissolution issues in radioactive waste at the U.S. Department of Energy's Hanford Site.

Chatterjee

The paper was authored by PNNL's **Dev Chatterjee** (lead), **Michele Conroy**, **Frannie Smith**, **Hee-Joon Jung**, **Zheming Wang**, **Reid Peterson**, **David Burtt**, **Eugene Ilton** and **Edgar Buck**, and **Ashfia Huq** of Oak Ridge National Laboratory.

NPSI measures its project accomplishments in terms of **Technical Advance**, **Business Impact** and **Operational Impact**.

Technical Advance

the event, which was sponsored by NPSI.

Dr. Navrotsky discussed some of her current research, including molten oxide solution calorimetry, a unique approach for understanding the thermodynamics of some refractory materials.

Dr. Navrotsky is interim dean of the UC-Davis College of Letters and Sciences' Department of Mathematical and Physical Sciences. She also directs the university's Nano and New Materials in Energy, the Environment, Agriculture, and Technology (NEAT) research group.

Her research interests have centered on relating microscopic features of structure and bonding to macroscopic thermodynamic behavior in minerals, ceramics, and other complex materials. Dr. Navrotsky has made major contributions to both mineralogy and geochemistry and to solid state chemistry/materials science in the fields of ceramics, mantle mineralogy and deep earth geophysics, melt and glass science, nanomaterials and porous materials.

NPSI-organized ACS Symposium Features Prominent Speakers, Attracts Solid Participation

The symposium, "Evolving Nanoparticle Reactivity Throughout Nucleation, Growth and Dissolution," was held April 5 at the 253rd American Chemical Society National Meeting & Exposition in San Francisco.

The symposium was organized by NPSI researchers **Michele Conroy**, **Frannie**

In this paper, NPSI staff investigated the potential role of chromium (Cr) on boehmite reactivity in caustic solution.

An important finding was that irrespective of the synthesis pathway, amount of Cr(III), or the resultant morphology, there was no evidence for Cr incorporation in the bulk structure, in agreement with quantum mechanics calculations. In fact, electron microscopic (EM) and spectroscopic analyses showed that Cr was enriched at the (101) edges of the boehmite. However, Cr had no measurable effect on the morphology during the synthesis step.

In contrast, comparison of the morphologies of the synthetic Cr-doped and pure boehmite samples after exposure to caustic solutions provided evidence that Cr inhibited the corrosion. Transmission electron microscopy (TEM) showed that Cr was not homogeneously distributed at the surface. Consequently, Cr may have partially passivated the surface by blocking discrete energetic sites on the lateral surfaces of boehmite.

Business Impact

Dissolution of aluminum (Al) phases is required to reduce the waste loadings in the final borosilicate glass waste form that will be used at the Hanford Waste Treatment and Immobilization Plant. Although not the most common Al-bearing species in the sludge, boehmite may become a rate-limiting step in the processing of the wastes.

Hanford boehmite is an order of magnitude more resistant to dissolution in hot caustic solutions than expected from surface-normalized rates. Data from actual waste samples has indicated that Cr is released into solution upon the dissolution of the bulk boehmite mineral phase. One hypothesis to be tested was whether this incorporation of this Cr had a retarding effect on the boehmite dissolution. These results suggest that Cr is not the most likely cause for slow actual

Smith, and **Jennifer Soltis**, and R. Lee Penn of the University of Minnesota.

Up to 40 people attended morning and afternoon sessions, listening to leading experts from across the U.S., as well as from Germany and Japan. Participants learned the latest information about research in areas ranging from metal sulfide nanoparticle formation to environmental impacts of the Fukushima Daiichi Nuclear Power Plant disaster. PNNL researchers provided updates on NPSI advances in aluminum geochemistry and other work.

The symposium was held as part of ACS's Geochemistry Division activities, but also was co-sponsored by the Colloid & Surface Chemistry, Environmental Chemistry, and Nuclear Chemistry & Technology divisions.

Some of the symposium speakers and organizers gathered for a photo at the event.

From left, NPSI's Jennifer Soltis, Michele Conroy and Frannie Smith

waste boehmite dissolution.

However, this work has suggested areas for future exploration associated with the mechanism for boehmite dissolution. In particular, the impact of agglomeration--or oriented attachment--and the resultant impact on dissolution rates. Identification of a route to achieve accelerated boehmite dissolution rates would open up new processing options for Hanford waste.

Operational Impact

A wide range of spectroscopic techniques were used as part of this investigation.

- X-ray diffractograms of the undoped and Cr(III) doped boehmite samples were performed. The diffractogram for prototypic samples indexed as pure boehmite with an orthorhombic unit cell (a ¼ 3.700 °A, b ¼ 12.227 °A, c ¼ 2.868 °A).
- The neutron diffraction (ND) results are consistent with the X-ray diffraction measurements.
- The vibrational spectrum of boehmite prototypic sample showed bands at 3275, 3080, 1189, 1068, 732, 608, and 465 cm-1.
- The Raman spectrum of the boehmite prototypic sample shows four weak and broad bands which are the distinguishing features for boehmite.
- XPS indicated the O/Al and hydroxyl: oxide ratios for the non-doped boehmite are 2.01 and 1.00, which are consistent with expected stoichiometric ratios.
- Scanning electron micrographs (SEMs) of prototypic sample show rhombic plates with a uniform size distribution.

organized the symposium, along with R. Lee Penn from the University of Minnesota.

LaGraffe and Cahill Join Initiative's Advisory Committee

Dr. David LaGraffe and **Dr. Christopher L. Cahill** have recently joined NPSI's Advisory Committee, a group of leading experts that provides guidance and leadership and research teams.

LaGraffe

Dr. LaGraffe is a retired Army colonel who currently serves as the Associate Assistant Deputy Administrator for Defense Nuclear Nonproliferation R&D in the Department of Energy's National Nuclear Security Administration.

Cahill

Dr. Cahill is a professor of Chemistry and International Affairs in the Department of Chemistry at The George Washington University. Other advisory committee members:

Karthik Subramanian - Chair
(Washington River Protection Solutions)
John Berg
(University of Washington)
Michael Demkowicz
(Texas A&M University)
Andy Felmy
(Washington State University)
Glenn Sjoden
(Air Force Technical Applications Center)
William Ulicny
(Department of Energy).

- The high resolution TEM shows the single crystal nature of the plates.

NPSI Team Makes Advance

Nuclear Fuel Research Cut Down to Size

By Lisa Staudinger

Until now, nuclear fuel studies could be conducted only in highly restricted facilities with costly, restricted technology by specially trained personnel.

These limiting factors vanished when NPSI's **Richard Clark** and his team made it possible to study important degradation processes in irradiated uranium oxide (UO2) in essentially any facility by any researcher with any relevant instrumentation.

The team's work on NPSI's Epsilon project has cut the nuclear fuel ATM-109 down to a size that is safer, less complicated to handle, and more versatile in its uses than ever before. This world-leading innovation could save millions of dollars while affording more researchers access to this area of study--now research institutions without Category-level facilities can study used nuclear fuel for the first time. Clark and his team have demonstrated a method of generating micron-size samples of radioactive material that makes it safer and cheaper to use in studies and offers collaborative opportunities never before possible.

The project has revived PNNL research active in the 1990s and extended it to create a new paradigm in nuclear materials characterization and handling. Their strategy of conducting materials science at the micron scale will allow more researchers to study nuclear fuel degradation in non-radiological facilities with a broader range of instruments.

PNNL staff who serve on the committee are **Chris Aardahl**, **Chris Mundy**, and **Dawn Wellman** (Committee Secretary).

NPSI Launches Two New Projects

NPSI launched two new projects at the beginning of fiscal year 2017, bringing the total number of active projects to 11.

Abrecht

NPSI's **David Abrecht** serves as the principal investigator for a new Science Thrust 1 project, *Development of Phase Field Modeling to Predict Morphologies of Plutonium Oxalate.*

In Science Thrust 3, **Greg Kimmel** is leading the other new project, *Development of a Rad AFM Capability*.

Kimmel

Recent NPSI Publications and Presentations

Journal Articles:

Devanathan, R. 2017. "Molecular Dynamics Simulation of Fission Fragment Damage in Nuclear Fuel and Surrogate Material," *MRS Advances.* Available online. DOI: https://doi.org/10.1557/adv.2017.9

Kessler S., D.G. Abrecht, R.A. Clark and J.M. Schwantes. 2016. "Vibrational Contributions to

Clark's team has been studying the formation of epsilon phase particles in used nuclear fuel since 2015. Epsilon phase particles are five metal phases resulting from the irradiation of UO2 fission products. Their formation can lead to point and line defects in the fuel, and eventually problems such as cracking. Researchers believe much of the same chemistry that causes epsilon phase particles may also be at work in corroding the first layer of containment surrounding nuclear fuel (called cladding). As dry storage of used nuclear fuel becomes more prevalent, cladding integrity becomes more important to confirm and preserve. The team's breakthrough sample preparation of ATM-109 smooths the path toward safe storage of used fuel and other useful applications.

The Epsilon project team developed a safer and less costly sample preparation method.

Staff Ingenuity. . .

NPSI Efforts Improve Accessibility to Instruments

Since NPSI's formation, one of the initiative's goals has been to find new ways to safely and more fully tap instrumentation and capabilities at PNNL to advance nuclear process science.

That objective was realized this past year when research staff developed a free release workflow that enables safe movement of minute radioactive samples from the Radiochemical Processing Laboratory to other facilities at PNNL

Phase Stability in the Mo-Ru System." *Journal of Alloys and Compounds*, Volume 689, pp. 969-976. DOI:http://doi.org/10.1016/j.jallcom.2016.08.071

Chatterjee S. M.A. Conroy, F.N. Smith, H.J. Jung, Z. Wang, D.G. Burtt, A. Huq, E.S. Ilton and E.C. Buck. November 2016. "Can Cr(III) Substitute for Al(III) in the Structure of Boehmite?" *RSC Advances*. DOI:10.1039/C6RA20234A.(See associated newsletter article in right column).

Presentations:

Conroy, M.A., K.L. Pellegrini, E.C. Buck, D.E. Perea, D.J. Edwards and R.A. Clark. 2017. "Epsilon Phase Fission Products in Spent Nuclear Fuel Cladding--A Complimentary Atomic Resolution Electron Microscopy and Atom Probe Tomography Study." Presented by Michele Conroy at the *Materials Research Society (MRS) Spring 2017 Meeting*, Phoenix, AZ, April 2017.

Isley W.C., S.M. Kathmann, Z. Wang, G.B.Hall, E.J. Bylaska, T.Q. Meadows and G.J. Lumetta. 2017. "Spectroscopic and Computational Characterization of Eu(III)-Oxalate Precipitation Processes." Presented by Will Isley at the *253rd National Meeting & Exposition of the American Chemical Society (ACS)*, San Francisco, CA. April 2017.

Pellegrini K.L., C.Z. Soderquist, R.A. Clark and J.M. Schwantes. 2017. "Radiochemical, Elemental, and Isotopic Analysis of Epsilon Phase Material from Irradiated Fuel." Presented by Kristi Pellegrini at the *253rd National Meeting & Exposition of the American Chemical Society (ACS)*, San Francisco, CA. April 2017.

Soltis J.A., M.A. Conroy, W.C. Isley, T.Q. Meadows, G.B. Hall, S. Chatterjee, Z Wang, S.M. Kathmann, J.J. De Yoreo, E.C. Buck, G.J. Lumetta. 2017. "Effect of Processing Conditions on Lanthanide and Actinide Oxalate Crystal Growth Mechanisms: Insights from In Situ Characterization and Computational Modeling." Presented by Jennifer Soltis at the *253rd National Meeting & Exposition of the*

for study, taking advantage of instruments not available in RPL.

The effort started with scientist **Dallas Reilly**. In studying requirements, Dallas brought to light an existing PNNL free release workflow document that's been on the books for some time but wasn't widely understood and was rarely used. The document enables easier, but safe, movement of miniscule samples outside of the RPL if certain thresholds, including Nuclear Regulatory Commission surface contamination limits, are met. Dallas socialized the process with research and facilities staff, and it has now been successfully used by Dallas and several colleagues.

In addition to Dallas, staff who helped advance the approach are **Jon Schwantes**, **John Cliff**, **Danny Perea**, **Arun Devaraj** and **Woody Buckner**, all of whom have been recognized with PNNL Outstanding Performance Awards.

NPSI Lead Sue Clark (center) recently recognized staff with awards for the free release workflow. Pictured with Sue from left are Arun Devaraj, John Cliff, Dallas Reilly and Danny Perea. Not pictured: Jon Schwantes and Woody Buckner.

American Chemical Society (ACS), San Francisco, CA. April 2017.

Devanathan R., M.A. Conroy and W. Jiang. 2017. "Atomistic Simulation of Swift Heavy Ion Irradiation Effects in UO2 and CeO2." Presented by Ram Devanathan at *TMS 2017 Annual Meeting*, San Diego, CA, February 2017.

Kessler, S.H. 2017. "Multi-Scale Modeling Efforts in the Chemical Processing of Nuclear Materials," presented by Sean Kessler to the *Oregon State University Chemical, Biological, and Environmental Engineering Seminar*, February 2017.

Chun, J. 2017. "Rheology of Dense Slurries: Toward Better Understanding via Correlations Between Scales," presented by Jaehun Chun, invited speaker, at Washington State University - Tri-Cities, February 2017.

New Video: PNNL's Radiochemical Processing Laboratory

This video provides the latest info on capabilities and projects at the Radiochemical Processing Laboratory at PNNL.

Radiochemical Processing Laboratory

STEM Provides a New Tool for Initiative Projects

Pacific Northwest National Laboratory has purchased a multi-million-dollar analytical scanning transmission electron microscope (STEM) that will be installed in PNNL's new Quiet Suite for high-end microscopy. The suite is located in the Radiochemical Processing Laboratory (RPL).

This new instrument is one of four microscopes that will revolutionize PNNL's micro-analytical characterization capabilities for studying radiological materials, and will be a resource for accomplishing NPSI research activities.

The STEM is an abberation-corrected (AC), cold field emission gun, 300kV JEOL Atomic Resolution Microscope (JEM ARM300CF). It comes equipped with a 4kx4k Gatan OneView™ CMOS CCD camera, two large-area x-ray energy dispersive spectroscopy detectors, and a Gatan Image Filter for electron energy-loss spectroscopy.

Brad Johnson, a manager in PNNL's Energy and Environment Directorate, led the effort to acquire the microscope and build the Quiet Suite. "This will be the second microscope like it in the U.S. And, in regard to studying radiological materials, it exceeds the analytical and atomic resolution capabilities of anything available at other national laboratories," he says.

NPSI researchers are looking forward to the new resource. "This device will greatly enhance the

study of nuclear materials and directly benefit NPSI projects that use microscopy. It will enable us to work with highly radioactive samples quickly and easily," says Scientist Edgar Buck, who leads a project investigating boehmite dissolution using in-situ liquid cell and cryo transmission electron microscopy.

In addition to supporting NPSI research, the new AC-STEM and RPL Quiet Suite will offer valuable capabilities that will be useful to sponsors who have needs to gain greater understanding of nuclear materials.

The RPL is a Hazard Category II Non-reactor Nuclear Facility. Along with other PNNL assets, the laboratory provides key state-of-the-art nuclear research resources of value to the nation.

PNNL-SA-125884

Nuclear Process Science Initiative
energyenvironment@pnnl.gov

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