Thursday Morning, November 10, 2022

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+AS+LS-ThM

Emerging Topics and Methods in Actinide/Rare Earth Science

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **Alison Pugmire**, LANL, **Paul Roussel**, AWE, UK

8:00am **AC+AS+LS-ThM-1 Nuclear Forensics 2020:A Strategic Inflection Point*, David Willingham,*** Lawrence Livermore Laboratory **INVITED**

The terrorist attacks of 9/11/01 greatly increased the visibility of nuclear forensics, as policy makers became increasingly concerned about the possibility of well-organized terrorist groups obtaining a nuclear weapon or dirty bomb.The Departments of Defense (DOD), Energy (DOE), Homeland Security (DHS), and State (DOS), as well as the Federal Bureau of Investigation (FBI) and the intelligence community, all play key roles in nuclear forensics. DHS, for example, was founded in November 2002 and included, from the start, a formal nuclear forensics program in its Science & Technology Branch.An August 2007 presidential decision directive established the specific roles these agencies would play and formally established the National Technical Nuclear Forensics Center (NTNFC) within DHS to coordinate planning, integration, assessment, and stewardship of the U.S. government's nuclear forensics capabilities. In 2010, the Nuclear Forensics & Attribution Act established a National Nuclear Forensics Expertise Development Program (NNFEDP) within the NTNFC aimed at "developing and maintaining a vibrant and enduring academic pathway from undergraduate to post-doctorate study in nuclear and geochemical science specialties directly relevant to technical nuclear forensics."National laboratories like LLNL have particularly benefitted from the establishment of postdoctoral fellowships.

In 2021, primary responsibility for nuclear forensics within the US Government transferred from DHS to the National Nuclear Security Administration (NNSA) within DOE with the issuance of National Security Presidential Memorandum 35, National Technical Nuclear Forensics. However, the Nuclear Forensics & Attribution Act of 2007 is still in force, which defines certain roles for DHS, particularly for stewardship of the nuclear forensics' workforce. Starting with the FY21 budget, there have been substantial increases in funding for NNSA for both nuclear forensic operations and R&D. However, the exact configuration of the nuclear forensics expertise development program(s) going forward is still being determined."

This talk will highlight some of the outstanding research conducted by our DHS postdoctoral fellows, including:

1. Development of RIMS as a tool for in situ analyses for nuclear forensics.
2. Improved determination of half-lives and branching ratios important for U rad-chem
3. Exploration of the use of isochrons for age dating of impure samples.
4. Development of new stable isotopic systems as new sources of signatures for nuclear forensics.
5. Development of rapid methods for dissolving solid samples

8:40am **AC+AS+LS-ThM-3 The Non-Integer Occupancy Ground State Hypothesis*, Miles Beaux,*** Los Alamos National Laboratory **INVITED**

A deeply ingrained and long-standing practice exists for identifying integer orbital occupancy ground state electronic configurations for neutral atoms of the elements. For certain elements, the identification of the electron occupancies of the orbitals in a neutral atom can be a controversial topic, instigating heated debate among scientists. The pedagogy of how atomic structure and the periodic table are initially taught might serve as a driver for this practice. For example, the octet rule is often used to explain the most energetically favorable ionic states, similarities in properties of like-group elements, and the most stable compounds formed by the transfer and sharing of electrons. However, the octet rule is also insufficient to explain the existence, structure, and properties of transition metal elements, including the lanthanides and actinides.

A more fundamental quantum-based understanding of electronic structure provides a firm basis for the overall structure of the periodic table. Specifically, the octet rule is understood as the stability of completely filled *s*-, and *p*-orbitals each having electron capacities of two (l=0; m_l=0; m_s=±½) and six (l=1; m_l=-1,0,+1; m_s=±½), respectively, with each Period, *n*, having n_s and n_p orbitals (except for Period 1, for which no 1*p* orbital exists). Extrapolation of this quantum mechanical underpinning of the Periodic Table explains the existence of the *d*- and *f*-blocks. The filling patterns of the orbitals for elements in the Period Table reveals relative energies of the various orbitals. Deviations from the filling pattern are often explained to varying degrees of satisfaction by the interplay between Hund's rule and the Aufbau principle for near-degenerate states; the stability of empty, half-filled, and completely filled orbitals; and core level screening. As the energy landscape for electron orbitals becomes more crowded for higher Period elements, the potential for near energy degenerate states increases. The potential for quantum superposition of electrons in these near energy states leading to effective non-integer orbital occupancies will be discussed in the context of observed instabilities in actinide and rare earth elements. Experimental and theoretical efforts to investigate this hypothesis for a series of Np, Pu, and Am compounds will also be described.

9:20am **AC+AS+LS-ThM-5 Legacy Plutonium at the Hanford Site*, Edgar Buck*,** *D. Reilly, G. Hall, K. Kruska, L. Liu, S. Triphathi, B. McNamara, A. Casella, D. Meier,* Pacific Northwest National Laboratory **INVITED**

The morphological characteristics of plutonium materials may provide information on the processes that were used to create the material; however, understanding of the detailed thermodynamic and kinetic processes needed to predict the evolution of its particle size distribution, crystal habit, and agglomerated state is still evolving. There has been an effort to fill this technical gap using an integrated experimental and modeling approach for formation of plutonium phases, including oxides and oxalates. Several different types of plutonium phases have been observed in wastes at the Hanford site, such as the Z9 crib near the former plutonium finishing plant and plutonium solids found in the SY102 and TX118 tanks. Laboratory experiments have been conducted to probe the formation mechanisms for these materials. By examining the preciptiating plutonium solids using a combination of in-situ optical microscopy (OM), scanning electron microscopy (SEM), cryo-electron microscopy (CryoEM) and in-situ transmission electron microscopy (TEM)., we have been able to demonstrate the occurrence of non-classical crystalline pathways for plutonium particle growth in some instances.

Understanding crystallization pathways in plutonium materials depends on the ability to unravel relationships between the intermediates and final crystalline products at the nanoscale, which is a particular challenge with radioactive materials. However, these powerful new tools of in-situ and cryoEM are providing new insights into the plutonium chemical system. The experimental data is helping to parameterize the computational modeling with the potential to lead to the development of predictive tools for identification.

11:00am **AC+AS+LS-ThM-10 Focused Ion Beam for Spatially Resolved Morphological Analysis of Nuclear Materials*, Brandon Chung*,** *S. Donald , D. Rosas, S. Sen-Britain, V. Som, N. Teslich, A. Baker,* Lawrence Livermore National Laboratory*; A. Ditter, D. Shuh,* Lawrence Berkeley National Laboratory

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. Conventional analysis using bulk nuclear material provides an overall analytical value, but a typical nuclear material is heterogeneous, requiring highly spatially resolved characterization. Consequently, averaging material characteristics may obscure critical forensic signatures resulting from local chemical and structural variations. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Our work shows the internal morphological and chemical variations in host nuclear materials provide valuable information about the material's production processes and recent environmental exposures. We identified that internal microscopic features entrapped within bulk nuclear materials contain trace elements or chemical that are attributable to their origin, processing, and environmental exposures.

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11:20am **AC+AS+LS-ThM-11 Studying Combined Influence of Alpha Irradiation and Dissolved Hydrogen on UO-$_2$ Corrosion Using a Microfluidic Electrochemical Cell**, ***Jennifer Yao**, B. McNamara, M. O'Hara,* Pacific Northwest National Laboratory*; N. Lahiri,* Pacific Northwest National Lab*; E. Ilton, C. Wang, E. Buck,* Pacific Northwest National Laboratory

It is well accepted concept that α-decay is the most important source of radiation in the spent nuclear fuel (SNF) after 1,000 years [1]. The influence of α-irradiation in the presence of dissolved H_2 on the corrosion of UO_2 can provide important information to assess the impact of the long-term SNF to the storage environment. However, experiments with bulk amount of SNF are expensive owing to the need for shielded hot cell facilities to protect researchers from the intense radiation field. To address this challenge, we employed a novel invention, particle-attached microfluidic electrochemical cell (PAMEC), to investigate UO_2 corrosion under different conditions (e.g., α-irradiation and H_2) at the microscale. Less than 10 µg of UO_2 (containing 1% to 10% $^{233}UO_2$) powder was mixed with polyvinylidene fluoride (PVDF) and carbon black to form the working electrode and included into PAMEC, which ^{233}U was used as alpha source to simulate the"aged" spent fuel [2]. The response of the corrosion potential of a ^{233}U contained UO_2 working electrode to dissolved H_2 in 0.1 M $NaClO_4$ (pH=9.5) will be presented. In addition, the 50nm thick Si_3N_4 detection window on PAMEC allows in situ imaging of the corrosion process using the high-resolution imaging technique, such as scanning electron microscope (SEM) coupled withEnergy-dispersive X-ray spectroscopy (EDS). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO_2 electrode that was exposed to alpha radiation and dissolved H_2. Our work demonstrates the study of combined influences on UO_2 corrosion under the conditions that are known to be present in the long-term SNF environment by employing a microfluidic electrochemical cell. We vision this approach can be widely applied to study the influences of conditions that resemble the practical repository environment on SNF, while with greatly reduced hazardous risk when performing such experiments.

References:

(1) Ewing, R. C., Long-term storage of spent nuclear fuel. *Nature Materials* **2015,***14*, 252-257. 10.1038/nmat4226

(2) Carbol, P.; Cobos, J.; Glatz, J.-P.; Ronchi, C.; Rondinella, V.; Wegen, D. H.; Wiss, T.; Loida, A.; Metz, V.; Kienzler, B.; Spahiu, K.; Grambow, B.; Quinones, J.; Martínez Esparza, A., *The effect of dissolved hydrogen on the dissolution of 233 U doped UO 2 (s), high burn-up spent fuel and MOX fuel*. 2005; p 140.

11:40am **AC+AS+LS-ThM-12 A Model to Extract the Size-Dependent Surface Structure of Actinide Oxide Nanoparticles**, ***Shinhyo Bang**, L. Moreau,* Washington State University

Characterization of actinide oxides at the nanoscale presents unique challenges due to their radioactivity, high surface area, and inherent diffraction broadening due to small grain size. Extended x-ray absorption spectroscopy (EXAFS) is an analytical method to investigate atomic-scale structural properties that enables their encapsulation and does not rely on long-range order. There is a limitation that EXAFS only gives the averaged structural information of heterogeneous samples. We aimed to deconvolute EXAFS results to extract the surface coordination environment of UO_2 NPs by proper modeling, and investigate how it evolves with varying sizes (1.4, 4.7, 8 nm). The termination effect was used to quantify the surface terminating species of UO_2 NPs. A higher degree of oxygenation on the surface was observed for 8 nm NPs. EXAFS simulation was implemented to backtrack the surface structure of these NPs. It was observed that the bond contraction due to the surface relaxation effect was localized in a few outermost layers of NPs and the surface disorder of 1.4 and 4.7 nm NPs was significantly enhanced from that of bulk.

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