Actinides and Rare Earths Focus Topic
Room On Demand - Session AC-Invited on Demand
Actinides and Rare Earths Invited On Demand Session

AC-Invited on Demand-7 Identifying Structural Features That Result in Activation and Coupling of Vibrational Modes in Actinyl Materials*, Tori Forbes,* University of Iowa **INVITED**

Vibrational spectroscopy is a valuable characterization tool for actinide chemistry and provides important information on bond strength, oxidation state, and coordination environment.This is particularly true for high valent actinides, where the actinyl cation ($D_{\infty h}$) possesses symmetric and asymmetric stretching modes that are typically Raman and Infrared active, respectively.Complexity is introduced by lowering the symmetry of the actinyl moiety, which can cause activation of modes within the spectral window of interest.In addition, coordination of the actinyl cation by equatorial ligands or intermolecular interactions in the solid state can result in concerted motions that lead to unexpected signals within these systems. In this presentation, I will focus on the spectral analysis of neptunyl (NpO_2^+/NpO_2^{2+}) and uranyl (UO_2^{2+}) solid-state compounds and explore activation and vibrational coupling effects of these materials.Surface effects for both solid crystalline phases and U(VI) adsorption onto electrospun polymer fibers will also be discussed.

AC-Invited on Demand-13 Sulfur Containing Ligands for Actinide Separations: How Do They Work?*, Jenifer Shafer,* Colorado School of Mines **INVITED**

Trivalent actinide lanthanide separations are amongst the most beguiling on the periodic table. A typical approach to accomplishing these separations is the use of soft donors which preferentially interact with the actinides over the lanthanides. Certain sulfur containing ligands are very effective at accomplishing these separations, but not all sulfur donating ligands are effective at this separation. Consequentially, a spread from very limited to record breaking separation efficacy can be observed despite very limited adjustment to the sulfur electronic structure in some instances. Recent studies presented here suggest the solvation environment surrounding metal-ligand complex is a very relevant design optimization point when developing actinide-lanthanide separations based upon sulfur-donating ligands. This presentation will discuss three vignettes that compare aqueous sulfur donors, aryl dithiophosphinic acids and Cyanex 301 and how their metal-ligand interactions occur. These ligand systems will allow for the development of a preliminary design framework of relevant separations features for actinide-lanthanide separations using sulfur ligands.

AC-Invited on Demand-19 Tracking Uranium Speciation by Synchrotron Spectromicrosopy*, Jesse Ward,* Pacific Northwest National Laboratory **INVITED**

Synchrotron techniques have several attractive features for application in a nuclear forensics context. Soft X-ray spectromicroscopy can yield chemically-sensitive and element-specific information about particles at a sub-micron scale. Hard X-ray fluorescence (XRF) imaging shows greater sensitivity to trace elements compared to electron microscopy techniques, at a similar spatial scale, and does not require extensive sample preparation. This talk will present the results of a ~2-year study using scanning transmission X-ray microscopy (STXM) to track the physical and chemical changes in uranyl fluoride particles stored under different relative humidity conditions. In addition, this talk will present the initial results of a more recent study comparing XRF and electron microprobe analysis data from uranium particles with varying trace element profiles. These projects demonstrate some of the unique capabilities synchrotron facilities can bring to the field of nuclear forensics.

AC-Invited on Demand-25 The PreCalc Project: Multiscale Framework for Predicting Morphology of Plutonium Oxide Particles*, Lindsay Roy,* Savannah River National Laboratory **INVITED**

Nearly all of the plutonium in the world has been manufactured synthetically through large-scale separation and purification facilities.The different processes create specific isotopic, chemical, and physical characteristics, or signatures, and those can be organized to determine whether an interdicted nuclear sample is or is not consistent with a given process.One of the most common processes is the conversion of plutonium nitrate to oxide through Pu(IV) oxalate precipitation process. Recently it has been shown that the morphological and physicochemical signatures produced from laboratory-scale experiments do not translate linearly to the production process because inhomogeneous temperature and pressure gradients dramatically complicate the macroscopic picture.It is our assertion that multi-scale, multi-physics models can provide a basis for the prediction of specific properties, but the approach must capture the atomistic features of nonequilibrium dynamic phenomena at finite temperatures while maintaining relevance at the process scale.

In that context, this presentation will be an overview of the modelling efforts at SRNL to integrate multiple time/length scales for a description of the precipitation and calcination dynamics of PuO_2 from a production facility, entitled the PreCalc Project.This presentation will discuss the framework development and modeling progress thus far in the project.

AC-Invited on Demand-31 Chemical and Microstructural Analysis of Nuclear Fuels at Nano-Length Scale Using Atom Probe Tomography*, Mukesh Bachhav,* Idaho National Laboratory **INVITED**

Understanding the microstructural and chemical changes in irradiated metallic and oxide fuel is integral to research and development of fuel cycle programs. Fissioning of uranium isotope in metallic and oxide nuclear fuel produces about a hundred primary fission fragments, many of which are unstable and thus generate still other isotopes through their chains of decay. Chemical analysis on fission product is crucial in understanding the behavior for their long-term use in reactor. For instance, fission products such as noble gases xenon and krypton are retained within bubbles and pores in the fuel material. However, certain fraction is released into the free volume of the fuel rod, which can be a potential life-limiting phenomenon in nuclear fuel rods. Such a build-up of rod internal gas pressure can severely affect the integrity of fuel cladding. Thus, swelling behavior and fragmentation of the fuel is associated with types of fission products formed during fission process.It is therefore essential to determine the chemical nature of fission products formed in U based fuels in order to predict its long-term behavior under extreme irradiation and temperature condition. More often, these microstructural changes associated with irradiation of fuels takes place at nano-length scale. There are very few analytical techniques in the field of materials characterization, which can quantify chemical composition and correlate to their spatial distribution at near atomic scale.

In recent past, Atom Probe Tomography (APT) has established itself to be an effective technique for elucidating 3D chemical composition in materials at nanoscale for a wide range of structural materials used for nuclear application. Thanks to advances in laser assisted APT, sample preparation methods in shielded glove box and programing tools, APT is now reliably used to correlate microstructure, microchemistry and property changes in nuclear materials. APT datasets provide 3D atom-by-atom reconstructions of nanoscale volumes with isotope identification and has emerged as a highly effective technique, complementing the information from more established microscopies. In this study, we present detailed analysis on correlation of fission products to burnup of nuclear fuel using APT technique on two U based fuels (Metallic: U-Mo and oxide- UO_2). For metallic fuel, systematic analysis is carried out on low enriched U-Mo alloy with burnup of 52 % and 69 % for fission product analysis.Similar method used to determine the burnup gradient in UO_2 fuel pin, which possess thermal gradient across radial direction influencing the formation and migration of fission products. These results provided insight into fundamental understanding of fission products in ceramic and metallic nuclear fuels.

AC-Invited on Demand-37 Surface Properties of Actinide Dioxides; Crystal Growth and Catalysis*, Enrique Batista,* *G. Wang, D. Gonzalez, P. Yang,* Los Alamos National Laboratory **INVITED**

Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictate aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stem from surface interactions with environmental species. Similarly, the morphology of crystal growth conditions is dictated by the stabilization or destabilization of different surfaces by ligands present in the solution environment. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this talk we present results of these studies for a series of actinide dioxides (AnO_2). We show how, under predicted conditions, one can control the morphology of growth, starting from nanoparticles to solids. The effect of surface defects is also analyzed as they can significantly affect the outcome, not only in morphology but also on the catalytic properties of the different exposed surfaces.

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