control of large U⁺ and UO₂⁺ ion formation as a function of static ToF-SIMS Ga⁺ primary ion bombardment parameters. We report the observation of large U⁺, UO⁺, and UO₂⁺ ions (x = 1-14) during 25 keV Ga⁺ analysis of the DU surface oxide and sputter cleaned metal surface during primary ion bombardment under static conditions. These ions are large enough to suggest that intact cleavage from the DU surface is energetically prohibitive. Rather, collision cascade theory suggests that these large species are the product of post-ionization reactions in the selvedge of DU [4]. Here, we report variation in the power law fits of secondary ion counts of U⁺, UO⁺ and UO₂⁺ ions as a function of x (x = 1-7) due to sputtering 2 nm into the DU surface oxide at ion current densities varying from 20 pA to 20 nA. We also report the variation of power law fits to secondary ion counts of U⁺ ions as a function of x (x = 1-14) due to tuning of instrument cycle time. Finally, we observe different rates of conversion of U⁺ ions to UO⁺ as a function of x in in-chamber surface oxidation under UHV conditions from residual moisture during static spectrum collection over a period of 3000 s. Future applications of this work include monitoring of ion formation and variation in recombination reactions in the presence of oxygen, water vapor, and temperature. This work was also performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.


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**Actinides and Rare Earths Focus Topic**

**Room On Demand - Session AC-Contributed On Demand**

**Actinides and Rare Earths Contributed On Demand Session**

**AC-Contributed On Demand-1 Characterization of Uranium Oxide Corrosion Using a Microfluidic Electrochemical Cell, Jennifer Yao, E. Buck, S. Tripathi, N. Lahiri, E. Ilton, S. Riechers, D. Reilly, Pacific Northwest National Laboratory; S. Chatterjee, TerraPower LLC; X. Yu, Pacific Northwest National Laboratory.**

Study of UO₂ corrosion is important in understanding the spent nuclear fuel (SNF) disposal. To address the challenges in investigating large amount of SNF materials, we developed a new approach to incorporate UO₂ powder onto the working electrode of a microfluidic electrochemical cell, aka the system for analysis at the vacuum liquid interface (SALVI) E-cell, to facilitate UO₂ corrosion study at the microscale. Instead of using bulk spent fuel pieces as working electrode at the macroscale, UO₂ powder was mixed with polyvinylidene fluoride (PVDF) and carbon black to form the working electrode with mm dimension and included into the SALVI E-cell. The UO₂ powder electrode went through electrochemical corrosion in 0.1 M NaClO₃ (pH=9.5) aqueous electrolyte using the electrochemical station. Multimodal imaging analysis, including in situ scanning electron microscope (SEM) coupled with Energy-dispersive X-ray photoelectron spectroscopy (EDS) as well as ex situ transmission electron microscope (TEM) and atomic force microscopy (AFM), was applied to reveal the morphological change, oxidation layer distribution, and topographical information of UO₂ before and after corrosion. In addition, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO₂ electrode surface disassembled from the microfluidic E-cell after anodic oxidation. Our results demonstrate a promising approach to characterizing UO₂ corrosion at the microscale using multimodal imaging. Particularly, in situ SEM imaging and EDS mapping allow direct observation of corrosion in liquid. This new approach is useful in studying the interaction between geological repository environments (e.g., groundwater and SNF) to validate and improve the Fuel Matrix Dissolution Model.

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**AC-Contributed On Demand-4 Observation of Multiple Dirac States in a Magnetic Topological Material EuMg₂Bi, Firoza Kabir, University of Central Florida; M. Hasen, University of Central Florida; F. Cheenicode-Kabeer, A. Apers, Uppsala University, Sweden; X. Ding, Idaho National Laboratory; G. Dhakal, K. Dimitri, C. Sims, S. Regmi, L. Persaud, University of Central Florida; K. Gofryk, Idaho National Laboratory; P. M. Oppeneer, Uppsala University, Sweden; D. Kaczorowski, Polish Academy of Sciences, Poland; M. Neupane, University of Central Florida.**

Initiated by the discovery of topological insulators, topologically non-trivial materials, more specifically topological semimetals and metals have emerged as new frontiers in the f eld of quantum materials. In this work, we perform a systematic measurement of EuMg₂Bi, a compound with antiferromagnetic transition temperature at 6.7 K, observed via electrical resistivity, magnetization and specific heat capacity measurements. By applying this technique to the recently discovered EuMg₂Bi, we were able to determine the signature of 5f-electronic correlation effects in the theoretical X-ray spectra. We found that the Pu 5f-6dhybridization effect provides an extra channel to mix the j=5/2 and 7/2 orbitals in the 5f valence. As a consequence, the resultant electron occupation number and spin-orbit coupling strength deviate from the intermediate coupling regime. We have also applied this approach to the 5f-phase of Pu.

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**AC-Contributed On Demand-16 EXAFS as a Probe of Actinide Oxide Formation in the Tender X-Ray Regime, James Tobin, University of Wisconsin-Oshkosh; S. Nowak, SLAC National Accelerator Laboratory; S. Yu, Lawrence Livermore National Lab; R. Alonso-Mori, T. Kroll, D. Nordlund, T. Weng, D. Sokaras, SLAC National Accelerator Laboratory.**

Recent developments in Resonant Inelastic X-Ray Absorption Spectroscopies such as XAS have been a powerful tool to reveal the valence electronic structure when assisted with theoretical calculations. In this work, we employed the DFT+Gutzwiller rotationally-invariant slave boson method to obtain the local Hamiltonian of the single-impurity Anderson model (SIAM), and used exact diagonalization (ED) method to calculate the XAS spectra from the model. An in-house built computational code was developed for the ED method. By applying this technique to the recently discovered 5f-electron topological Kondo insulator plutonium tetraboride (PuB₄), we were able to determine the signature of 5f-electronic correlation effects in the theoretical X-ray spectra. We found that the Pu 5f-6dhybridization effect provides an extra channel to mix the j=5/2 and 7/2 orbitals in the 5f valence. As a consequence, the resultant electron occupation number and spin-orbit coupling strength deviate from the intermediate coupling regime. We have also applied this approach to the 5f-phase of Pu.

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**AC-Contributed On Demand-5 The Observation of Large Uranium Oxide Cluster Ions from the Surface of Depleted Uranium Under Static Bombardment Using Ga⁺ During ToF-SIMS, Shoshin Sen-Britain, A. Nelson, Lawrence Livermore National Laboratory.**

Laser ablation (LA) mass spectrometric and static time-of-flight secondary ion mass spectrometry (ToF-SIMS) of metals produces similar ion distributions of large M₂O₄⁺ ions due to gas phase recombination reactions of small M₂O₄⁺ ions in the gaseous cloud formed during LA, or selvedge formed in static ToF-SIMS during ion sputtering [1]. Specifically in the case of depleted uranium (DU), an expanded understanding of these recombination reactions due to ion sputtering under vacuum and in the presence of oxygen or in atmosphere can further our understanding of nuclear forensics and debris analysis [2, 3]. We describe here precise
Plutonium has a complex electronic structure, where the role of the 5f orbitals in chemical bonding and the level of covalency has not been understood in detail and is a very active field of research. Resonant inelastic X-ray scattering (RIXS) is a valuable tool and can lead to a deeper understanding of the electronic structure of plutonium materials.1 Also high-energy resolution X-ray absorption near edge structure (HR-XANES) has proven powerful in plutonium speciation studies.2,3

Relativistic quantum chemical computations for the Pu4+ ion and the PuO2 compound were performed. We will discuss four computational measures of covalency of the Pu 5f orbitals. The PuM4-5-edge HR-XANES and PuM4-5-edge core-to-core 3d4f RIXS on PuO2 and other Pu4+ compounds under various experimental conditions were conducted at the INE and ACT beamlines at the Karlsruhe research accelerator (KARA) at KIT in Karlsruhe Germany.4,5

We found that for PuO2 the Pu 5f covalent mixing with O valence orbitals overall is relatively small. It is the largest in the 5f(7/2) a1 orbit with the highest orbital energy. The analysis of the Pu M4-5-edge HR-XANES in combination with the calculated results, showed that the spectra cannot be described with a simple one electron transition between individual 3d and 5f orbitals applying the dipole selection rule. There is considerable amount of redistribution of 5f electrons involved in both the Pu M4-5-edge and the Pu M5-7-edge absorption processes, i.e. shake-up excitations (I = 5f(5/2) to 5f(7/2)) take place. From the comparison of the computational results with the HR-XANES spectrum, it was found that the second peak in the Pu M4-5-edge and the shoulder feature in the Pu M5-7-edge spectrum are probing the 5f(7/2) a1 orbital and are therefore expected to be sensitive to bond variations. It will be discussed how the different interatomic interactions affect the Pu M4-5-edge core-to-core 3d4f RIXS map of PuO2. The here presented spectroscopic and theoretical tools will help to advance the understanding of the electronic structure of Pu materials.

Acknowledgement: We acknowledge funding from the European Research Council (ERC) (grant agreement n° 101003292). We thank the Institute for Beam Physics and Technology (IBPT), KIT for the operation of the storage ring, the KARA.


We overcome the presented challenge through focusing on the study of ultrasmall nanoparticles, which present particularly high surface area to volume ratios. The high percentage of surface atoms makes bulk characterization techniques such as X-ray absorption spectroscopy (XAFS) become surface-sensitive probes, enabling us to resolve surface structure in atomistic detail. New models will be presented that provide an indication of elemental speciation of surface atoms and sites for surface ligand bonding through combination of geometric models with structural parameters extracted from XAFS. Results obtained through this work are broadly applicable towards resolving nanoparticle surface chemistry and provide foundational methodology towards exploring the nanoscale properties of actinide oxides.

AC-Contributed On Demand-25 Broadening of the XPS Spectra of U Oxides, C. Nelin, Consultant; Paul S. Bagus, University of North Texas

It is common to attempt to improve the energy resolution of XPS in order to obtain more information about the electronic structure of the system studied. However, it may not be possible to improve the resolution because unresolved final states features are present which lead to broad features. These unresolved features may arise from closely spaced multiplets for the angular momentum coupling of the core and valence open shell electrons. They may also arise from excitations to higher lying vibrational levels for the final ionic states which may be especially important when bond distances for the core-ionized states are very different from those for the initial state; see, for example, Ref. [1]. When the energy separation of the final states are less than or comparable to the lifetime of the core-hole, it will not be possible to resolve the states and there will only be a broadening, often quite significant, for the observed peak composed of these unresolved features. Thus, for example, the U5f2/2 peak of UO2 has a FWHM of 1.4 eV although the instrumental resolution was 0.3 eV. [2] Similar large FWHM have been observed for U in different oxidation states. [3] In order to be able to relate the widths of these broadened features to the chemical and physical interactions in the system, it is necessary to understand the separate contributions of the multiplet splittings and the vibrational excitations. It has been shown that, for U(VI) 4f XPS in UO2, the contributions of the multiplet splitting and the vibrational excitations are comparable, each contributing ~0.5 eV to the FWHM. [2] In the present work, the contributions of these mechanisms are examined for U(V) and U(VI) oxidation states. In addition, the broadening is examined for the XPS of different core levels where the relative importance of multiplet and vibrational broadening is different from that for the U(4f) XPS. The theoretical predictions for these different parameters can be validated paving the way to extract chemical information from the measured FWHM. [4] The theoretical framework for these predictions is based on wavefunctions for embedded cluster models of the oxide.


AC-Contributed On Demand-28 XPS, UPS Study of Pure and Alloyed U Hydrides, Oleksandra Koloskova, E. Tereshina-Chitirova, M. Paukov, Charles University, Prague, Czech Republic; T. Goudier, European Commission, JRC; Institute for Transuranium Elements, Germany; J. Kolarcic, Institute of Physics, Czech Academy of Sciences, Czechia; L. Havela, Charles University, Prague, Czech Republic

Besides the fundamental importance, uranium hydrides have considerable relevance for nuclear energy and devices, which motivates continuous effort to understand its formation and properties [1], in particular its electronic structure. Photoelectron Spectroscopy is a method which directly probes the electronic structure. However, surface oxidation is an issue, which we overcome using the strategy of thin film synthesis. Surprisingly, it became possible to stabilize the UH2+ phase (non-existent as a bulk) in a thin film form [2].

XPS was first used for analysis of the samples quality. One of the difficulties is that the H-Ls line is a part of the U-valence band, hence it cannot be used to quantify the H concentration. We followed an empirical approach based on gradual increase of H2 partial pressure in the working gas (Ar) while
monitoring variations of the U-$4f$ core-level spectra until saturation is reached [3].

Details of electronic states in the vicinity of the Fermi level are explored by UPS, surpassing XPS both by intensity and energy resolution (about 70 meV). Comparison of UPS spectra of U and UH$_3$ revealed that the spectra are similar just at the Fermi level (if properly normalized), the maximum for UH$_3$ is slightly displaced from the Fermi level to $\approx 140$ meV binding energy. The U metal has DOS increasing up to the Fermi level and the Fermi-Dirac cutoff forms the maximum at 90 meV. Another feature of UH$_3$ (UH$_3$ is very similar) is the broad shoulder at 0.5 eV (ascribed to 5$f$ multiplet from GGA+U calculations). Details of the DOS shape resist to a quantitative description using DFT calculations [1]. However, spectral density obtained from DMFT calculations captures both the maximum just below $E_F$ and the 0.5 eV shoulder. This stresses the importance of electron correlations for the description of U hydrides.

As the XPS spectra of UH$_3$ and UH$_3$ are so similar, it is hard to distinguish which species was deposited. Magnetization measurements turned particularly useful. While both species are ferromagnets, their $T_c$ values are different (165 K for UH$_3$ and 120 K for UH$_3$) [2]. Using the $M(T)$ dependence, we can assess the phase composition (pure UH$_3$, UH$_3$ or mixed-phase) of the samples.

This work was supported by the Czech Science Foundation under the grants No. 18-02344S and 21-09766S and by the Grant Agency of the Charles University under Project No. 814120.

References

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 also be discussed.

This work was supported by the Czech Science Foundation under the grants No. 18-02344S and 21-09766S.

References
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

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 PuO₂ 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

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 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 programming 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: UO₂). 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 UO₂ 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.
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