Actinides and Rare Earths Focus Topic
Room 103C - Session AC+AS+SA-ThM
Chemistry and Physics of the Actinides and Rare Earths

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Art Nelson, Lawrence Livermore National Laboratory

8:00am **AC+AS+SA-ThM1 Covalency in Oxidized Uranium*, James G. Tobin,*** University of Wisconsin-Oshkosh **INVITED**

Actinides, the 5*f* elements and their compounds, alloys, and mixtures, are a crucially important part of modern technological societies. Moreover, uranium dioxide is the most widely used nuclear fuel for the generation of electricity. Yet, because of the complexity of the 5*f*/6*d* electronic structure in the actinides, a fundamental understanding of their physical behavior, in actinides in general and uranium dioxide in particular, has not been achieved.

Theoretically, it has been proposed that covalency is an important part of the electronic structure of actinide dioxide, although some disagree. Experimentally, spectroscopic studies have been reported which support the hypothesis of 5*f* covalency. However, a crucially important and absolutely essential component has been missing: a systematic study where the nature of the oxidant is changed, so the specifics of the 5*f* and 6*d* covalencies could be varied and monitored. The turning-on and turning-off of an effect is the essence of a true benchmarking. The work reported here clearly and irrevocably establishes experimentally the strong presence of U 5*f* –O 2*p* covalency in the unoccupied density of states of UO2, the most important of our nuclear fuels.

This comparative study will feature the isoelectronic systems uranium dioxide (UO2) and uranium tetrafluoride (UF4). While isoelectronic, both being U^{+4} $5f^{\,2}$ in the formal limit, they exhibit substantially different structures. UO2 is a fluorite (cubic) material, while UF4 is monoclinic. However, both exhibit very similar U *L*3 extended x-ray absorption fine structure (EXAFS) behavior, indicative of quantitatively similar interatomic distances. The result of this comparative study is that UF4 exhibits continued 6*d* covalency but the almost complete loss of 5*f* covalency, while UO2 clearly displays both strong 5*f* and 6*d* covalencies. Here we have direct experimental demonstration that 5*f* covalency is important in actinide oxides but can be lost with a more powerful oxidizing agent such as fluorine.

To summarize: Using x-ray emission spectroscopy and absorption spectroscopy, it has been possible to directly access the states in the unoccupied conduction bands that are involved with 5*f* and 6*d* covalency in oxidized uranium. By varying the oxidizing agent, the degree of 5*f* covalency can be manipulated and monitored, clearly and irrevocably establishing the importance of 5*f* covalency in the electronic structure of the key nuclear fuel, uranium dioxide.

Collaborators on this work include: S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng. [*See PHYSICAL REVIEW B **92**, 045130 (2015)]

8:40am **AC+AS+SA-ThM3 An In Situ X-ray Diffraction Study of Plutonium Oxidation*, Paul Roussel,*** *W. Lake,* AWE, UK

X-ray diffraction was used to follow the oxidation of α-phase plutonium in oxygen at a pressure of 500 mbar. The composition of the growing oxide scale consisted of the trivalent cubic sesquioxide α-Pu_2O_3 and tetravalent fluorite dioxide PuO_2. The hexagonal β-sesquioxide phase was not detected. The quantity and lattice parameters of the oxide phases were determined from Rietveld analysis of the diffraction patterns. The lattice parameters of both oxides were found to decrease with increasing oxide quantity. Decreasing lattice parameters occur from increasing oxygen anion concentration in each oxide phase. The rate of oxidation for the total oxide composition at various temperatures below 100 °C was found to be linear, indicative of possible moisture enhanced oxidation. A detailed analysis of the contributions of the individual oxide compositions will be presented. Post oxidation optical microscopy of the coherent oxide scale showed areas of thicker scale typical of island growth. When the oxidation reaction was allowed to proceed to form olive green spalled oxide, X-ray diffraction analysis of the powder showed it to consist as a mixture of both cubic oxide phases.

Our initial XRD work presented at this meeting in 2012 suggested the initial oxide film grown on δ-plutonium might be amorphous. This work has been repeated using the XRD in-situ environmental reaction cell and the results will be presented.

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9:00am **AC+AS+SA-ThM4 Advanced Applications of Synchrotron Sources to Describe Water Soluble Plutonium Colloids*, Thomas Dumas,*** CEA, France*; E. Dalodière, M. Virot,* ICSM Marcoule*; V. Morosini,* CEA Marcoule*; T. Chave,* ICSM Marcoule*; C. Hennig,* Helmholtz Zentrum Dresden-Rossendorf*; T. Wiss,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements*; D.K. Shuh, T. Tyliszcaak,* Lawrence Berkeley National Laboratory*; P. Moisy,* CEA Marcoule*; I. Nikitenko,* ICSM Marcoule

Colloidal species of Pu(IV) were shown to play a central role in the speciation of plutonium in various aqueous wastes and in biosphere [1-3]. However, a comprehensive understanding of the behavior and structure of Pu colloids remains elusive and hinders progress on the development of reliable processes of their management. Preparation of plutonium colloidal species with controlled composition and properties is still a challenge. Herein, we report the preparation of stable Pu(IV) colloids by the action of ultrasonic waves on PuO_2 in salt-free water conditions. Sonochemical colloid was compared with hydrolytic colloid using HRTEM, Pu LIII-edge EXFAS and STXM/NEXAFS techniques.

HRTEM revealed nanostructured morphology for both colloids composed of particles of PuO_2 (*fcc*, space group) measuring about 7 nm and 3 nm, respectively. The EXAFS spectra of colloidal PuO_2 nanoparticles were fitted on the basis of PuO_2 cristal structure. Combined HRTEM and EXAFS results revealed the correlation between the coordination numbers (i.e. Pu-O and Pu-Pu) and atomic surface-to-volume ratio of studied PuO_2 nanoparticles.

The STXM/NEXAFS technics implemented at ALS BL 11-0-2 was used for the first time to study plutonium colloids. It offers a new topographic angle to describe colloids combined to spectroscopic measurements at oxygen K edge. It first revealed that the oxygen state of hydrolytic Pu colloid is influenced by hydrolyzed Pu(IV) species in much more extend than the sonochemical colloids. Moreover the topographic analysis highlight discrepancies in plutonium and oxygen distribution for hydrolytic Pu colloid on the contrary to sonolitic one.

Complementarily to previous studies, this work confirmed that plutonium colloids (hydrolytic and sonochemical) can be described as core-shell nanoparticles composed of quasi stoichiometric PuO_2 core and hydrolyzed Pu(IV) moieties at the surface shell. Nevertheless, the application of soft X-ray technics highlight the strong influence of the synthetic route on colloid chemical composition and hence its expectable reactivity.

1. A. B. KERSTING, Plutonium Transport in the Environment, *Inorg. Chem.,***52**, 3533 (2013).

2. A. I. ABDEL-FATTAH, D. ZHOU, H. BOUKHALFA, S. TERIMALA, S. D. WARE, A. A. KELLER, Dispersion Stability and Electrokinetic Properties of Intrinsic Plutonium Colloids: Implications for Subsurface Transport, *Env. Sci. Technol.*, **47**, 5626 (2013).

3. C. WALTER, M. A. DENECKE, Actinide Colloids and Particles of Environmental Concern, *Chem. Rev.,* **113**, 995 (2013).

9:20am **AC+AS+SA-ThM5 *In Pristinum* Observation of Plutonium Hydride*, Martin Brierley,*** *J.P. Knowles,* AWE

The reaction of plutonium with hydrogen creates plutonium hydride in an energetic process which often liberates the reaction product as a powder. Plutonium hydride is pyrophoric; therefore study of the reaction product usually requires that it is passivated by careful exposure to oxygen prior to removal from the reaction chamber. The passivation process is highly energetic with the potential to significantly affect the microstructure of the reaction product and surrounding metal. In this study we used a scanning electron microscope with an adjoining reaction chamber to maintain vacuum between reaction and analysis to grow plutonium hydride and subsequently analyse the reaction products as formed.

Initial work on electro refined Pu gave a slow reaction to hydrogen, requiring an *in situ* heat treatment to form hydride. Analysis of the reaction product was made *in vacuo* following reaction, preventing oxygen from accessing the sample. Subsequent cross sectional analysis of the reaction product morphology was performed, showing a coating of a hydride product layer with an open structure under the original surface oxide [1].

A sample of mixed α/δ phases was successively exposed to hydrogen for increasing durations of 60, 7200 and 70320 s. No evidence of reaction was evident following the 60 s and 7200 s exposures, unlike that observed in experiments on gadolinium [2] and uranium [3]. Following the 70320 s exposure, 96 % of the available hydrogen was consumed and several large anisotropic reaction sites had formed. The hydride sites on this mixed phase sample exhibited anisotropic growth similar to δ-stabilised plutonium samples investigated previously [4]. Deformation of the δ-phases surrounding hydride sites occurred via slip processes. Cracks formed in the overlying oxide layer above the deformed material allowing facile access for hydrogen to reach fresh Pu at the metal/oxide interface. Subsequent cross sectional analysis revealed anisotropic growth of hydride reaction sites, strongly supporting our previously proposed mechanism for anisotropic growth [4]. The α-phase domains resisted deformation and instead transferred the stresses from the hydride reaction front further into the surrounding metal. Post experimental cross sections through reaction sites suggest that hydride regions associated with α-domains had not undergone complete reaction.

References

1. M. Brierley et al., Journal of Nuclear Materials 469 (2016) 39-42

2. G.M. Benamar, et al., Journal of Alloys and Compounds 520 (2012) 98–104.

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4. M. Brierley, et al., Journal of Nuclear Materials 469 (2016) 145-152

9:40am **AC+AS+SA-ThM6 Evidence for f- and d-orbital Mixing in Lanthanide and Actinide Dialuminides, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, Pu)***, **Stefan Minasian**,* Lawrence Berkeley National Laboratory (LBNL)*; A.B. Altman, J. Arnold,* University of California at Berkeley*; E.D. Bauer,* Los Alamos National Laboratory*; C.H. Booth, J.I. Pacold, C.D. Pemmaraju, D.G. Prendergast, D.K. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory (LBNL)

For most scientific and technical applications, aluminum is well-regarded as a trivalent, electropositive and Lewis-acidic metal. However, this textbook model fails to adequately explain the unusual chemical and physical properties of many f-element molecules, materials, and alloys incorporating aluminum and other group 13 elements. In order to develop a more nuanced model of aluminum electronic structure, we have turned to metal K-edge X-ray Absorption Spectroscopy (XAS), which is an established technique for evaluating electronic structure in bioinorganic and inorganic compounds. Pre-edge peaks in K-edge XAS correspond to bound state transitions between core and unoccupied orbitals. Therefore, by comparing pre-edge features to established references, information can be gathered on the electronic structure of a system and the orbitals involved in bonding. However, there is very little precedent for the measurement and interpretation of aluminum K-edge XAS for molecules and materials.

This presentation will describe our recent efforts to develop Al K-edge XAS as a probe of chemical bonding and electronic structure in Al molecules and materials with lanthanide and actinide metals. Work began by examining a series of molecular aluminum compounds and by systematically varying supporting ligands and oxidation states. Features in the Al K-edge spectra were fully assigned through a comprehensive polarization study and comparison with the results of XCH and DFT calculations. Results were interpreted within a molecular orbital framework, providing unique insight that could not be obtained from analysis of NMR or metrics from single-crystal X-ray diffraction. These results have laid a foundation for ongoing efforts with lanthanide and actinide aluminum alloys, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, and Pu). Comparisons between the Al K-edge spectra and earlier resonant X-ray emission spectra for the MAl_2 compounds provide unique insight into how electronic structure influences the desirable physical properties of these materials. For $EuAl_2$ and $YbAl_2$, the increasing occupancy of the 4f orbitals enhances screening of the 5d orbitals, resulting in enhanced Al 3p and Ln 5d orbital mixing for Eu and Yb that is not observed for Ce, Sm, or Lu. For UAl_2 and $PuAl_2$, the Al K-edge XAS and theory results also provides convincing evidence of Al 3p and 6d orbital mixing. Because of the enhance radial extension of the 6d orbitals, 6d orbital involvement in bonding for $PuAl_2$ is more likely to have an impact on the stability of the Pu–Al bonds. Current efforts are focused on evaluating f-element interactions with aluminum in other stoichiometric and non-stoichiometric alloys.

11:00am **AC+AS+SA-ThM10 Comparative Analysis of Uranium Oxide Films***, **Miguel Santiago Cordoba**,* Los Alamos National Laboratory

Depleted Uranium (DU) Oxide thin films are considered to be employed as surrogates and reference compounds for systematic studies on the elucidation of fundamental properties of actinide materials. The goal of this work is to compare surface morphologies of DU oxide thin films fabricated by two techniques, polymer assisted deposition (PAD) and electron beam evaporation (EBE). In this contribution, we utilized a MultiMode atomic force microscope (AFM) operating in tapping mode in order to compare and establish a contrast among the three dimensional surface structures of polycrystalline U_3O_8 and UO_2 films fabricated by PAD, and UO_2 thin films deposited by EBE. Differences in surface morphology are analyzed, and the information provided by AFM is compared against other complementary techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Reported results revealed that films fabricated by both techniques had granular structure, with morphologies strongly depending on the fabrication methods and conditions.

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11:20am **AC+AS+SA-ThM11 Soft X-ray Spectroscopy of Actinide Materials***, **David Shuh**, S.G. Minasian, C. Pemmaraju, A. Canning, D.G. Prendergast,* Lawrence Berkeley National Laboratory*; T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley*; A. Modin, S. Butorin, J. Nordgren, L. Werme, P. Oppeneer,* Uppsala University, Sweden

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale. An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state.

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