# Tuesday Morning, October 30, 2012

**Actinides and Rare Earths Focus Topic**
**Room: 6 - Session AC+EN-TuM**

**Energetic Materials Issues for Nuclear Power: Fuels, Corrosion and Waste Disposal**
**Moderator:** J.G. Tobin, Lawrence Livermore National Laboratory

8:00am **AC+EN-TuM1 Novel Concepts for Enhanced Metallic Nuclear Fuel Performance**, *J.R. Kennedy, R.D. Mariani, D.L. Porter, S.L. Hayes, H.J.M. Chichester,* Idaho National Laboratory*, A.E. Wright, Y.S. Kim, A.M. Yacout, G.L. Hofman,* Argonne National Laboratory*, R.P. Omberg, D.J. Senor*, Pacific Northwest National Laboratory **INVITED**
The Advanced Fuels Campaign of the Fuel Cycle Research andDevelopment (FCRD) program of the Office of Nuclear Energy (DOE/NE) ischarged with the mission to develop and qualify fuel forms that can be used 1)to close the nuclear fuel cycle, 2) to increase fuel performance in reactor,and 3) be accident tolerant. In thefirst case, metallic fuels composed of (U,Pu,Np,Am)Zr alloys are beingdeveloped with the intention to transmute the transuranic isotopes in fastspectrum reactors. In the second case, increasing fuelperformance, fuel forms are being developed that may, for example, allow higherlevels of burnup in either fast spectrum or thermal spectrum reactors (lightwater reactors - LWR). In the finalcase, fuel forms that have an inherently higher level of tolerance to offnormal conditions are being developed in response to the Fukushima Daiichiaccident. A number of innovativeconcepts will be presented with respect to the above including decreased fuelsmear densities, annular fuel forms, cladding coatings or liners to preventfuel-cladding chemical interactions, gas vented fuel pin designs, advancedfabrication methods such as fuel-clad co-extrusion, U-Mo based fuel alloys,and, of particular interest to this session's topical area, targeted fuel alloyadditions into the actinide fuel composition that will sequester rare earthfission product migration to the fuel-cladding interface. Rare earth fission products have beenimplicated in enhancing detrimental fuel-cladding chemical interactions. These fuel development activities are a collaborationof Idaho National Laboratory with Argonne National Laboratory and with PacificNorthwest National Laboratory.

8:40am **AC+EN-TuM3 Low Temperature Oxidation of Plutonium: A Mott-Cabrera Mechanism**, *P. Roussel*, AWE, UK*, A.J. Nelson*, Lawrence Livermore National Laboratory **INVITED**
X-ray photoelectron spectroscopy was used to study the oxidation of d-stabilized plutonium between 190K and 300K. The gas-solid reaction on this highly reactive surface depends on the surface energy, electronic structure and temperature along with radiological dissociation of the $O_2$ molecule. The initial oxidation of sputter cleaned Pu metal by $O_2$ forms $Pu_2O_3$ followed by formation of $PuO_2$ on the $Pu_2O_3$ surface. Angle-resolved measurements indicate that the $PuO_2$ layer thickness is limited to 1.2 nm after continued $O_2$ dosing at the lower temperatures. These results suggest the Mott-Cabrera mechanism of oxidation at low temperature where the rate limiting step is the diffusion on O⁻ anions through the oxide film to the oxide/Pu interface increasing only the thickness of the $Pu_2O_3$ layer.

This work was performed under the auspices of the U.S. Dept. of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:40am **AC+EN-TuM6 The Sputtering Yields of Depleted Uranium and Uranium Carbide Bombarded and Alloyed by Either 30 keV Gallium or 16 keV Cesium Ions**, *W.J. Siekhaus, N.E. Teslich, P.K. Weber*, Lawrence Livermore National Laboratory
A sample of depleted uranium was abraded with 1200 grid SiC paper and subsequently polished with 3µm and 1µm diamond to a mirror finish. Areas 20µmx20µm wide that included uranium carbide inclusions were ion-etched with 30 keV Gallim ions with a current of 2.8 nA, for up to 5 minutes. The depths of the "craters" thus generated were measured by electron microscopy and by profilometry and the ratio of the number of uranium atoms removed and the ion fluence was used to determine the sputtering yield for both uranium and uranium carbide.

We show the results in SEM images of sputtered areas and depth measurements on "craters" that include uranium carbide inclusions.

The same procedure was used to determine the sputtering yield of 16keV Cesium ions bombarding uranium. At their respective energies the depth of penetration of Gallium and Cesium (109Å and 50Å, respectively, as calculated by the TRIM[1] code) is much smaller than the crater depths.

The measured depth increases represent therefore the sputtering yields of the Uranium-Gallium and Uranium-Cesium alloys created by ion implantation, since sputtered atoms originate almost inclusively from the first atomic layers of the substrate[2] . Comparison of the measured sputtering yields with those of pure U using Matsunami's equation[3] demonstrates the effect of alloying on sputtering yield.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

[1] Sputtering by Particle Bombardment. Behrisch, R. Ed. Springer Verlag GmbH., 2007.

[2] Burnett, J.W. et al., Journal of Vac. Science & Technology A., **6,** 3, 2064-2068, 1988.

[3] Matsunami, N. et al., Atomic Data and Nuclear Data Tables, **31,** 1-80, 1984.

10:40am **AC+EN-TuM9 Actinide Subsurface Chemistry in Waste Isolated Pilot Plant, Recent Development**, *M. Borkowski, J.-F. Lucchini, M.K. Richmann, D.T. Reed*, Los Alamos National Laboratory
Waste Isolation Pilot Plant (WIPP) is designed to permanently dispose radioactive waste generated by the US defense program. Waste is placed in a salt bed 2150 feet below the ground level. During the regulatory time repository may be filled with brine and interaction of brine components with actinide is objective of the Actinide Chemistry Repository Science Program. One of the brine components is borate (up to ~160 mM), present in the brine by the dissolution of Borax mineral. Borate chemistry especially in basic media is still unknown and in this study the interesting borate speciation in the basic media is presented. Recently it was reported that neodymium, analog for trivalent actinides, is complexed by tetraborate ion with log K ~4 and that plutonium forms a stronger complexes than that of neodymium. Also neptunium (V) forms complexes with borate and spectrophotometric evidence will be presented. Further investigations of borate chemistry and borate complexing properties are also discussed. Complexation power of different polyborate forms may be different. Some are able to form a covalent bond but other forms can only atract cation by a weak electrostatic interaction. Borate provides a wide range of pH buffering capacity from 6 to 12.

11:00am **AC+EN-TuM10 XPS Study of Uranium Oxides with Various Precipitating Agents**, *K.S. Holliday*, Lawrence Livermore National Laboratory*, J. Plaue,* University of Nevada, Las Vegas*, W.J. Siekhaus, A.J. Nelson*, Lawrence Livermore National Laboratory
X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES) are powerful tools for materials characterization by determining chemical shifts in core level spectra. By combining XPS data with the X-ray excited Auger transitions one is able to have a two dimensional analysis based on both initial state effects and final state relaxation energies. Specifically, combining the chemical shift of the U NOV Auger lines with the chemical shift of the U 4f photoelectron lines defines the Auger parameter (difference in the binding energy of the photoelectron and Auger lines) and results in a reliable method for determining oxidation states independent of calibration. Here, XPS analysis of core-level excitation and X-ray excited Auger transitions were combined to determine the Auger parameter and produce chemical state (or Wagner) plots for various uranium and thorium compounds. In addition this method is combined with valence band spectra to characterize uranium oxides precipitated with different reagents. The calcination of these precipitates is followed at various temperatures in an effort to identify unique characteristics associated with the precipitating reagent.

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