Actinides and Rare Earths Focus Topic
Room 103C - Session AC+MI-WeA

Actinide and Rare Earth Theory (2:20-3:40 pm)/Nuclear Power, Waste Remediation and Applications (4:20-6:20 pm)

Moderators: Paul Bagus, University of North Texas, Leon Petit, Daresbury Laboratory, UK, Alexander I. Landa, Lawrence Livermore National Laboratory, Melissa Denecke, University of Manchester, UK, David Geeson, AWE, UK, Stefan Minasian, Lawrence Berkeley National Laboratory (LBNL)

3:00pm **AC+MI-WeA3 First-Principle Calculations of Magnetic Properties of Actinide Complexes***, **Hélène Bolvin**,* IRSAMC, Université de Toulouse III **INVITED**

The calculation of properties of open-shell 5f molecules is a challenge for the methods of quantum chemistry : these complexes have many low lying configurations, spin-orbit effects are important and correlation effects must be taken into account. The SO-CASPT2 method gives results that compare well to experimental data : it is a two-step wave function based method. The multiconfigurational nature of the wave functions is described by starting with a CASSCF calculation, correlation effects are calculated by 2nd order theory and spin-orbit effects are introduced in the very last step by a state interaction procedure.

We will show by several examples how calculations have become a complementary tool to the experimental data in order to get information about the nature and the magnetization of the ground and excited states.

1. calculation of EPR parameters : the ground state and excited states of actinyl complexes depend strongly on the nature of the equatorial ligands. All calculations are rationalized using a model based on crystal field theory. [1,2,3]

2. calculation of the susceptibility of aquo An(III), An(IV), An(V) and An(VI) cations and comparison to the LS coupling scheme. [4]

3. calculation of the pNMR shifts in the An(Et-DPC) $_3^{3-}$ series and comparison with the lanthanide series. The variation in temperature of this shift will be discussed.

[1] D. Paez Hernandez, H. Bolvin J. Electron. Spectrosc. Relat. Phenom. 194, 74 (2014).

[2] F. Gendron, D. Paez Hernandez, F. P. Notter, B. Pritchard, H. Bolvin, J. Autschbach Chem. Eur. J. 20, 7994 (2014).

[3] F. Gendron, B. Pritchard, H. Bolvin, J. Autschbach Inorg. Chem. 53, 8577 (2014).

[4] M. Autillo, L. Guerin, H. Bolvin, P. Moisy, C. Berthon Phys. Chem. Chem. Phys. 18, 6515 (2016).

4:20pm **AC+MI-WeA7 Observations of Actinide-mineral Precipitation in Solution by *In Situ* Electron Microscopy***, E.C. Buck, **Michele Conroy**, J.A. Soltis,* Pacific Northwest National Laboratory **INVITED**

In this presentation, the history of Pu contamination at the Hanford site will be reviewed, including the various disposal locations, the quantities of Pu and co-contaminants disposed, and recent research efforts designed to unravel the chemical form of Pu in the environmental samples. Microanalytical information will also be presented for the sediments at the Z-9 site. The information will include the chemical characterization of the sediments at two bore holes drilled at the Z-9 sites. Although the majority of the plutonium is present as oxide, using both electron microscopy (EM) and x-ray absorption spectroscopy evidence was found for the formation of nano-sized mixed Pu and iron phosphate hydroxides that are structurally related to rhabdophane-group minerals. The Pu-phosphate formation may depend on the local microenvironment in the sediments, availability of phosphate, and hence the distribution of these minerals may control long-term migration of Pu in the soil. The presentation will also focus the role of *in-situ* EM can play in understanding nanoparticle formation and its subsequent interaction with substrates.

Iron (II) minerals, when in isolation, will control the fate of Pu; however, in a sediment with clay, calcite, and other soil minerals present as we observed in the Z9 sediments, other phases and elements may have a significant impact on the Pu chemistry. Nevertheless, the complexity found in the natural environments may lead to the formation of phases that may not be predicted in laboratory set-ups. Understanding the chemistry of Pu in complex media requires tools that can probe micro-environments. We have been exploring the use of *in-situ* EM to investigate the precipitation of Pu. All designs of cells for *in-situ* electron microscopy incorporate a membrane that prevents evaporation of the liquid sample in the microscope vacuum. We will describe other observations of Pu behaviour, morphology, and compositional changes studied with these new EM methods.

5:40pm **AC+MI-WeA11 PES Study of Surface Passivation in U-Zr Alloys***, **Ladislav Havela**, M. Paukov,* Charles University, Prague, Czech Republic*; F. Huber, T. Gouder,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements

High temperature *bcc* structure of Uranium (γ-U) can be retained to low temperatures by alloying with different *d*-metals. Such alloys are used, due to enhaced resitance to radiation damage and better mechanical properies comparing to α-U, as nuclear fuels. Alloying leads also to reduced surface reactivity. Such "stainless" uranium is much more resitant to oxidation, and reaction with hydrogen gas needs high H_2 pressures. This raises questions about phenomena at the surface of such alloys. We performed a photoelectron spectroscopy study of the alloy $U_{0.80}Zr_{0.20}$, prepared by rapid solidification (splat cooling). The concentration of 20% Zr was chosen as the lowest concetration which still gives a safe margin for single-phase *bcc* phase. In particular, we studied the properties of the surface exposed to oxidation and/or annealing.

The surface in the initial state is Zr-rich (approx. 85% Zr), and the Zr excess is only slowly removed by Ar-ion sputtering. In the cleaned state the U-4*f* spectra indicate that the degree of the 5*f* localization is not changed between the α-U and γ-U phases, which can be understood considering that the U-U spacing even in the γ-U phase remains far below the Hill limit. Also the valence-band spectra in UPS exhibit only small differences with respect to pure U, which adopts the α-U phase.

Exposing the clean surface of $U_{0.80}Zr_{0.20}$ to O_2, one observes relatively rapid oxidation. The dose of 5 Langmuir of O_2 converts 35-40% of metal into a dioxide, while Uranium oxidizes slightly more than Zirconium.

Isochronal annealing for 900 s leaves the clean surface unchanged for temperatures below 500 K. However, above this temperature the concentration of Zr in the surface layer fast increases. Repeated cleaning and annealing cycles lead to the same picture of surface enriched by Zr. The oxide formation of such surface is much more sluggish. This is true particularly for U, which has difficulty to form UO_2. The oxidation can be stimulated by elevated temperatures, pointing to the fact that such oxidation is modulated by diffussion of O thrugh the Zr overlayer. Still for 100 L of O_2 at 473 K the large part of U remains in metallic state and the amount of oxide is lower than for room-temperature oxidation of stoichiometric surface after 5 L O_2. The finding demosntrates that the U-Zr alloys are coated by Zr or Zr-rich film when exposed to 500-600 K and such film leads to a passivation of the surface.

This work was supported by the Czech Science Foundation under the Grant 15-01100S. The work at ITU was supported by the European FP7 TALISMAN project, under contract with the European Commission.

6:00pm **AC+MI-WeA12 XPS and SIMS Study of the Surface and Interface of Aged C^+Implanted Uranium***, **Art Nelson**, S. Donald, J. Siekhaus,* Lawrence Livermore National Laboratory

Core-level photoelectron spectroscopy in combination with X-ray excited Auger peak energies were blended with secondary ion mass spectrometry depth profiling to investigate the surface and interfacial chemistry of oxidized C^+ ion implanted polycrystalline uranium exposed to air for over 10 years at ambient temperature. Implantation of 33 keV C^+ ions into U^{238} with a dose of 4.3×10^{17} cm^{-3} produced a physically and chemically modified surface layer that was characterized and shown to initially prevent air oxidation and corrosion of the uranium. The evolution of the previously characterized surface and interfacial layers were now examined by using a combination of the C KLL and U NOV Auger peak energies with the associated chemical shift of the C 1s and U 4f photoelectron lines that defines the Auger parameter resulting in a reliable method for conclusively determining oxidation states independent of binding energy calibration. Results showed definitive Auger line-shapes and were used to produce a chemical state (Wagner) plot for select surface oxide and interfacial carbide. In addition, valence band spectra were used to explore the electronic structure of the aged carbide surface and interface layer. Furthermore, the time-of-flight secondary ion mass spectrometry depth profiling results for the aged sample confirmed an oxidized UC layer over the carbide layer/U metal interface.

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

Author Index

Bold page numbers indicate presenter