Thursday Afternoon, November 3, 2011

Actinides and Rare Earths Focus Topic
Room: 207 - Session AC+TF-ThA

The Structure, Properties and Chemistry of Thin Films of Actinides and Rare Earths
Moderator: L. Havela, Charles University, Czech Republic

2:00pm **AC+TF-ThA1 Plutonium Sorption and Reactivity at the Solid/Water Interface**, ***M. Schmidt***, *P.A. Fenter, S.S. Lee, R.E. Wilson, L. Soderholm*, Argonne National Laboratory **INVITED**

Reliable long-term predictions about the safety of a potential nuclear waste repository must be based on a sound, molecular-level comprehension of the geochemical behavior of the radionuclides. We apply *in situ* crystal truncation rod (CTR) measurements and resonant-anomalous X-ray reflectivity (RAXR) in combination with alpha-spectrometry to elucidate the sorption behavior of tetravalent actinides on muscovite under varying solution conditions.

Key retention mechanisms, particularly in clay formations, are surface mediated processes. In order to be able to understand these processes analytical techniques that allow selectively probing the mineral/water interface and elucidating processes at the interface under *in situ* conditions are required. X-ray reflectivity techniques (CTR, RAXR) have proven to be valuable tools for geochemical studies concerning the sorption behavior of metal ions [1] . More recently they have also been applied to study the sorption behavior of actinides [2] .

From CTR measurements the complete adsorption structure, consisting of adsorbed water and the ions adsorbed as inner sphere, outer sphere or extended outer sphere complex can be derived. RAXR extends this approach by providing elemental specificity to the CTR measurements, thus characterizing the contribution of a particular element to the structure.

Using a purpose-built sample cell for radiological experiments, X-ray reflectivity data was collected *in situ* from muscovite ($KAl_2[(OH,F)_2|AlSi_3O_{10}]$) in contact with the actinide-bearing solutions varying in composition (ionic strength, actinide concentration and speciation, background electrolyte). The data is complemented by precise quantitative analysis by means of alpha-counting experiments. The results clearly show the strong influence of the actinides' aqueous chemistry on their sorption behavior. It will be shown that a full description of the sorption behavior requires parameters such as the hydration enthalpy, complexation constants, hydrolysis constants, and polymer formation constants. At low actinide concentrations the formation of hydrated surface complexes is observed in good agreement with the large hydration enthalpies of the highly charged ions. At large excess of background electrolyte sorption occurs under preservation of the complexation by the anion. When a threshold metal ion concentration is exceeded sorption of polymers is observed which grow up to 150Å in size, while covering only small fractions of the surface.

1. Fenter, P., Reviews in Mineralogy and Geochemistry 2002, 49, 149-220.

2. Fenter, P.; Lee, S. S.; Park, C.; Soderholm, L.; Wilson, R. E.; Schwindt, O., GCA, 2010, 74, 6984-6995.

2:40pm **AC+TF-ThA3 Crystal Chemistry of Thorium Oxy Compounds Containing Tetrahedral Oxyanions**, ***A.J. Albrecht***, *P.C. Burns*, University of Notre Dame

Here we examine the crystal chemistry and structural topologies of Th compounds containing various cations that are coordinated by oxygen atoms in tetrahedral arrangements. We define the structural unit to be the part of the structure that consists of those polyhedra that contain higher valence cations, with an emphasis on their connectivity. In most cases, structures also contain interstitial units that balance the charge of the structural unit. In the compounds under study, which include both new structures and those from the literature, we find structural units ranging from clusters and chains, through sheets, to extended frameworks. The structural units in thorium compounds are of particular interest because they provide insights into the possible structures of compounds consisting of tetravalent transuranium cations, especially Np and Pu.

3:00pm **AC+TF-ThA4 Solution Route to High Quality Epitaxial Actinide Films Form Oxides to Carbides**, ***T.M. McCleskey***, *E. Bauer, A.K. Burrell, B.L. Scott, Q.X. Jia, T. Durakiewicz, J.J. Joyce, S.A. Kozimor, S.D. Conradson, R.L. Martin*, Los Alamos National Laboratory

We report on the solution based synthesis of epitaxial thin films of neptunium oxide and plutonium oxide. Actinides represent a tremendous challenge to first principle calculations of orbital energies due to the complicating features that arise from f orbital interactions. Theoretical development from first principle calculations relies on predictions of continuous materials with no boundaries. To test these theories requires experimental results using high quality single crystals. For many materials this can be a straight forward process. For actinide oxides the experimental work is complicated by the radioactivity that makes CVD processes challenging from a safety perspective and by the recalcitrant nature of the oxides. The challenge of modeling actinide oxides is best represented in Mott insulators such as UO_2. Theoretical calculations that worked with transition metals predict UO_2 to be a metal as opposed to an insulator with a 2.3 eV band gap. Recent reports predict the same metallic behavior for NpO_2. Many theoretical reports have highlighted the need for experimental work on single crystals. In the absence of single crystals they rely on work done on powders as in the case of PuO_2. We report here on epitaxial films of PuO_2 that are thin enough to measure the optical band gap directly. XRD has been used to determine the alignment of the PuO_2 relative to the substrate and EXAFS confirm the stoichiometry.

3:40pm **AC+TF-ThA6 U(VI) Uranyl Cation-Cation Interactions in Framework Germanates**, ***J.M. Morrison***, *P.C. Burns*, University of Notre Dame

The crystal structure determinations of four highly complex U(VI) germanate framework compounds reveal three distinct U(VI) sites—two that are coordinated by five equatorial oxygen atoms each to form pentagonal bipyramids and one that is coordinated by six oxygen atoms to form a distorted octahedron without the uranyl ion [1]. This is uncommon as most inorganic U(VI) compounds contain the uranyl ion, $(UO_2)^{2+}$. Also present are cation-cation interactions which occur when an oxygen atom of the uranyl ion also acts as an equatorial oxygen atom in a neighboring U(VI) polyhedron. CCIs are present in fewer than 2% of U(VI) compounds. Finally, a disordered system with the possibility of a one-dimensional GeO_5 chain has led us to suggest three structural models with regard to Ge coordination. The interesting structural and chemical complexities of these CCI-bearing compounds will be presented along with a discussion of the densities of CCI-bearing U(VI) compounds.

[1] Morrison, J.M.; Moore-Shay, L. J.; Burns, P.C. *Inorg. Chem.* **2011**, 50, 2272-2277.

4:20pm **AC+TF-ThA8 The Crystal Chemistry of Uranyl Selenates and their Relations with Uranyl Sulfates**, ***E.M. Wylie***, *P.C. Burns*, University of Notre Dame

Uranyl sulfate minerals have been studied for several decades owing to their importance in understanding ore genesis, as well as the interaction of uranium mine and mill workings with the environment. In contrast, no uranyl selenate minerals have been described, although several uranyl selenites are known. We are exploring the crystal chemistry of synthetic uranyl selenates produced under mild hydrothermal techniques. We have obtained crystals of several compounds and characterized them with single-crystal X-ray diffraction. They contain a sheet of edge-sharing uranyl pentagonal bipyramids and selenate tetrahedra that is topologically identical to those found in the zippeite group of uranyl sulfate minerals. These synthetic materials provide further insights into layered uranyl phases, including the relationships between the configurations of the structural sheets and their corresponding interlayer complexes. These structures will be placed in the context of known synthetic and natural uranyl sulfate and selenate compounds.

4:40pm **AC+TF-ThA9 Radiation-Induced Degradation of Photoluminescence in YAG:Ce**, ***S.G. Gollub***, *D.G. Walker, S.L. Weeden-Wright*, Vanderbilt University

Thermographic phosphors are ceramic based materials whose photoluminescence is temperature dependent. We fabricated the phosphor YAG:Ce to determine its sensitivity and selectivity to various radiation environments. In particular we investigated the effects of non-ionizing radiation on the photluminescent spectra. No change to the spectrum was observed after exposure to 1 MRad of x-ray radiation. Because x-rays are typically ionizing, we did not expect to see any significant degradation. When the material was bombarded with protons, which are know to cause displacement damage in many materials, a degradation was observed. Results of damage cross section and stopping power were commensurate with predicted values using SRIM. Results are shown as a function of proton energy and dose.

5:00pm **AC+TF-ThA10 The Behavior of Uranyl Peroxide Pyrophosphate Nanoscale Cage Clusters in Aqueous Solution**, ***K.L. Pellegrini***, *P.C. Burns, J. Szymanowski, J. Ling, J. Qiu*, University of Notre Dame

Twenty-six nanoscale cage clusters built from uranyl polyhedra have been reported to self-assemble in aqueous solutions over a range of pH conditions [1]. All contain peroxide groups that bridge between uranyl polyhedra, and some contain additional linkages such as pyrophosphate and oxalate. The focus of the current study is the U24P12 cluster that consists of 24 uranyl hexagonal bipyramids and 12 pyrophosphate groups. We have optimized the synthesis of this cluster to obtain pure yields. Subsequently, we have examined the behavior of the cluster in solution using electrospray ionization mass spectroscopy and small angle X-ray scattering. These studies are emphasizing the persistence of this cluster under a variety of conditions, as well as their aggregation in solution. Such materials are of considerable interest because of potential applications in an advanced nuclear energy system, including in fuel recycling. Results to date show that the U24P12 cluster persists in aqueous solution for several days under a range of conditions, and can be induced to aggregate via addition of various counterions.

1. Burns, P.C. *Mineralogical Magazine*. **2011**, 75, 1-25 Open Access on petercburns.com

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