

Actinides and Rare Earths Focus Topic Room 202C - Session AC+AS+SA-WeA

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Czech Republic, David Shuh, Lawrence Berkeley National Laboratory

2:20pm **AC+AS+SA-WeA-1 New Directions in f-Block Separations Chemistry based on Metal and Ligand Redox Activity**, *Eric Schelter*, *A McSkimming*, University of Pennsylvania; *J Su*, Los Alamos National Laboratory; *T Cheisson*, *H Fang*, University of Pennsylvania; *L Moreau*, Lawrence Berkeley National Laboratory, Berkeley; *B Cole*, *B Manor*, *M Gau*, *P Carroll*, University of Pennsylvania; *E Batista*, *P Yang*, Los Alamos National Laboratory; *C Booth*, Lawrence Berkeley National Laboratory; *Y Qiao*, *J Bogart*, University of Pennsylvania

INVITED

Chemical separations of mixtures of cations in the context of nuclear waste processing for lanthanide/actinide mixtures and ore processing of rare earth elements remain some of the most challenging to achieve selectivity.

We have been developing new or improved methods to address these challenges using redox chemistry. For example, by changing ligand characteristics it may be possible to attain unusual oxidation states, in the case of actinides, that would enable selective separations. This talk will include discussion of some of our efforts to manifest chemical distinctiveness in actinide redox chemistry and the associated electronic structures of such complexes. In a parallel effort, we have been developing separations chemistry for rare earth cations based on kinetic resolution.

Kinetic resolution has only rarely been applied in metal separations chemistry and represents an interesting new direction. Using a redox active ligand, a predictive system for inter-rare earth partitioning and separations will be described.

3:00pm **AC+AS+SA-WeA-3 Bond Distance Variations for Lanthanide and Actinide Compounds and its Implication**, *Tsuyoshi Yaita*, Japan Atomic Energy Agency, Japan; *S Suzuki*, *T Kobayashi*, *H Shiwaku*, Materials Sciences Research Center, Japan Atomic Energy Agency, Japan

INVITED

Lanthanide and actinide are f-electron filling series and the properties of the series on their chemical behavior are very similar if valence states are same, while an electronic configuration of the inner shell for each element is slightly different compared to the similarity in size, and the value of special elements such as Nd and Dy used as neodymium magnet is high in the use of high-tech products. Regarding actinides series, radiotoxic Am is paid for attention in the geological disposal of radioactive waste and the R&D for partitioning and transmutation technique is performed. Accordingly, intra-series separation for lanthanide and actinide with similarity in chemical behavior would be quite important for the recovery of noble metal used as high-tech parts and treatment of high-level waste prior to geological disposal, resulting that the development of useful separation system could improve economic efficiency and reduction of environmental load.

On these backgrounds, we focus on the intra-series separation for lanthanide and actinide, especially, the relationship between variation of separation efficiency in the series and systematics of structure and electronic structure, and then, we try to propose new separation concept. Especially, in this talk, we talk about the variation of hydration or complex bond distances for trivalent actinide and lanthanide series based on X-ray crystallography and EXAFS and the interpretation based on the SX-XAS/XES and theoretical calculation.

4:20pm **AC+AS+SA-WeA-7 Spectroscopic Studies of Trivalent Actinide Coordination**, *Benjamin Stein*, *M Kerlin*, *A Morgenstern*, *E Batista*, *S Bone*, *S Cary*, Los Alamos National Laboratory; *J Lezama Pacheco*, SLAC National Accelerator Laboratory; *S Kozimor*, *P Yang*, Los Alamos National Laboratory

INVITED

Radioisotopes have a rich history in medicine, with their use dating back to the earliest studies of radioactivity. Only recently, however, have α -particle emitting radionuclides been considered for medical applications. Targeted alpha therapy utilizes the unique properties of α -emitting radionuclides to selectively kill cancer cells, with the short range of α -particles causing minimal collateral damage to nearby healthy cells. Actinium-225 (^{225}Ac) has been identified by the Department of Energy Isotope Program Long Range plan as an isotope of high national interest for targeted alpha therapy, due to its favorable half-life (10 days) and 4 α -emissions in the decay chain.

However, if the ^{225}Ac is not securely bound to the targeting vector this

effectiveness results in very high toxicity to off-target (i.e. healthy) cells. Due to the high radioactivity and limited supply of all actinium isotopes, very little fundamental chemistry is known about this elusive element. Utilizing the unique radiological facilities at Los Alamos, we have been able to use microscopic amounts (~ 30 micrograms) of the longer-lived isotope actinium-227 (half-life of 22 years) for chemical studies. Utilizing this isotope, we have developed handling and containment techniques to perform "classic" spectroscopic and chemical studies in support of developing actinium chelates to advance the use of ^{225}Ac in targeted alpha therapy. During these studies of actinium coordination chemistry we have also made comparisons with the more "traditional" trivalent actinides, in particular americium and curium. We will discuss our latest EXAFS, NMR, and computational results on these difficult to handle elements by presenting a comparison of acetate and phosphonate binding, and how this informs chelator development.

5:00pm **AC+AS+SA-WeA-9 Speciation of Rare Earth Elements in Coal Harvesting Byproducts**, *Xu Feng*, *M Council-Troche*, *J Morris*, *A Noble*, *R Yoon*, Virginia Polytechnic Institute and State University

Rare earth elements (REEs) are critical for the development of renewable energy resources, national security, and advanced manufacturing. With the recent closure of the rare earth mine in California, the U.S. relies entirely on foreign imports mainly from China, which poses serious economical and national security concerns. According to a study commissioned by the National Energy Technology Laboratory (NETL), the U.S. coal and coal byproducts contain ~ 11 million metric tons of recoverable REEs, only a small fraction of which could satisfy the domestic need [1].

Recent USGS studies showed that the REEs in U.S. coals are preferentially partitioned to clay minerals [1], suggesting that the clay byproducts may be a major source of the critical materials. Ion-adsorbed REEs in clay appear to exist as two distinct forms: (1) ionic species adsorbed by coulombic attraction which is thought to be the primary form in REE-adsorbed clay deposits in South China, and (2) colloidal REEs formed by hydrolysis, each requiring a unique extraction strategy. However, the conditions under which the ion-exchange clays were formed in the U.S. coals and accompanying mineral matter may be different from those for the South China ion-adsorption clays, and the specific speciation of REEs in U.S. coal materials is currently unknown. It is, therefore, critical to study the fundamental mechanisms by which REEs are adsorbed on clay minerals in aqueous media to develop effective targeted extraction strategies.

In this work, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of representative light and heavy rare earth elements on artificial REE-adsorbed clay samples. Characteristic REE $3d_{5/2}$ features of the artificial clay sample, including the peak position of the two multiplet-split components, the magnitude of the multiplet splitting and the intensity ratio of each multiplet-split component, were compared to those of the high-purity REE standards such as $\text{REE}(\text{OH})_3$, REE_2O_3 and REECl_3 to provide insight into the identification of REE speciation on the artificial sample. XPS results suggest that $\text{REE}(\text{OH})_3$ is the primary REE species on the artificial REE-adsorbed clays. Furthermore, X-ray Adsorption Spectroscopy (XAS) was used to probe the speciation of representative light and heavy REEs in natural coal and coal byproduct samples by comparing the oxidation states and specific bonding environments to those of REE standard materials.

[1] Bryan, R. C., D. Richers, H.T. Andersen, and T. Gray, "Assessment of Rare Earth Elemental Contents in Select United States Coal Basins," Document No: 114-910178-100-REP-R001-00, January 2015.

5:20pm **AC+AS+SA-WeA-10 Exotic Electronic Properties of Strongly Correlated Compounds NpPd_3 and PuPd_3** , *Krzysztof Gofryk*, Idaho National Laboratory; *J Griveau*, *E Colineau*, Institute for Transuranium Elements; *K McEwen*, University College London; *W Nellis*, Harvard University; *J Smith*, Los Alamos National Laboratory

Actinides are characterized by the coexistence of localized and itinerant (delocalized) $5f$ -states near the Fermi energy. This dual nature of the $5f$ -electrons leads to many complex phenomena that are observed in these strongly correlated materials, spanning magnetic ordering, heavy-fermion ground state, unconventional superconductivity, and/or "non-Fermi liquid" state. The electronic properties of the strongly correlated electron systems are related to the formation, near the Fermi level, of a narrow band with large density of states and in spite of intensive theoretical and experimental efforts their nature is still not well understood. This behavior is well emphasized in $An\text{Pd}_3$ (An -U, Np, Pu) system. UPd_3 crystallizes in the hexagonal crystal structure and shows four phase transitions below 7.8 K, attributed to a succession of antiferroquadrupolar orderings of the

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uranium ions localized on the quasi-cubic sites of the $dhcp$ structure. Depending on a heat treatment, $NpPd_3$ crystallizes in hexagonal and cubic crystal structures. The hexagonal $NpPd_3$ (h - $NpPd_3$) exhibits two transitions at 30 and 10 K. It has been suggested that the low temperature transition might be due to ordinary antiferromagnetic ordering while the high temperature one might be caused by a quadrupolar order. The cubic $NpPd_3$ (c - $NpPd_3$) orders antiferromagnetically below 52 K and the magnetic and transport measurements suggests that the transition is first order. $PuPd_3$ crystallizes in the cubic structure and shows an antiferromagnetic order below 24 K. To explore the influence of electronic correlations on the physical properties in the $AnPd_3$ system, here we present our detailed magnetic, thermodynamic, and transport studies of $NpPd_3$ and $PuPd_3$. We show that all results obtained present characteristic behaviors of 4f- and 5f-electron strongly correlated materials. The magnitude and overall temperature dependence of the electrical resistivity, magnetoresistivity, Hall and Seebeck effect, and heat capacity of $NpPd_3$ and $PuPd_3$ are archetypal of materials with Kondo interactions. Our measurements also reveal an unusual magnetic ordering in c - $NpPd_3$. At T_N , the specific heat exhibits an extremely large peak [as large as 1000 J/(mol K)] and the magnetic susceptibility shows a clear jump. The transport properties of c - $NpPd_3$ indicate a dramatic reconstruction of the electronic structure at the Néel temperature, probably accompanied by a large change in the Fermi surface topology, which shows up as pronounced anomalies at this temperature in the electrical resistivity, the magnetoresistivity, and the Seebeck and the Hall coefficient. We will discuss implications of these results.

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