

# Tuesday Morning, October 31, 2017

## Actinides and Rare Earths Focus Topic

Room: 22 - Session AC+AS+SA-TuM

### Nuclear Power, Forensics, and Other Applications

**Moderator:** James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+SA-TuM1 Design of Synergistic Protein-ligand Systems for f-element Coordination, where Separation, Decontamination and Nuclear Medicine Meet, Rebecca Abergel, Lawrence Berkeley National Laboratory** **INVITED**

Separation of elements from the 4f- and 5f- series is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Understanding the fundamental bonding interactions between those metal centers and selective ligands presents a rich set of scientific challenges and is critical to the development of new separation strategies as well as to a number of applied problems such as the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific lanthanide and actinide coordination features by bio-inspired catecholamide and hydroxypyridinone hard oxygen-donor ligands. Using such ligands allows the solution differentiation of different metals through stabilization in specific oxidation states and provides information on their respective electronic structures. In addition, X-ray diffraction analyses using the mammalian iron transport protein siderocalin as a crystallization matrix revealed remarkable aspects of the protein's interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends in the later 5f-element sequence, when combined with theoretical predictions. These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of f-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications.

8:40am **AC+AS+SA-TuM3 Image Processing And Particle Analysis Of Fission-Truck-Analysis In Nuclear Forensic, Itzhak Halevy, Department of Physics, NRCN, Israel, U. Admon, (Retiree), IAEC-NRCN, Department of Materials, Beer-Sheva Israel, E. Chinea-Cano, Office of Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), Austria, A.M. Weiss, Faculty of Engineering, Bar-Ilan University, Israel, N. Dzigal, Office of Safeguards Analytical Services (SGAS), Austria, E. Boblil, Department of Physics, IAEC-NRCN, Israel**

Particle analysis is a key discipline in safeguards and nuclear forensic investigations, as well as in environmental research. The radioactive particles are usually in the micrometric size range, and intermixed within huge populations of other particles, like air-borne dust, soil, industrial exhaust pollutants or estuary sediments.

We are using the Fission Truck Analysis (FTA) technique. In that technique plastic detectors used for rapping a Lexan catcher with the particles and together are radiated in nuclear reactor with thermal neutrons. The Fission Truck are trucks done by the fission products. The fission material is dominant in producing the trucks, namely the <sup>235</sup>U isotope. The Fission Truck could be more visible by special etching and can be used to locate the particles.

From that point, the analysis of Fission Truck is an image processing. Scanning the detectors is a time-consuming procedure. Automated scanning and fission star recognition will make all the Analysis easier to quantify

The challenge, therefore, consists in scanning and imaging a relatively large area detector, at a resolution of about 1 μm, and locating the FT clusters while rejecting the artefacts.

Image processing was done using the Fiji distribution of ImageJ. The algorithms shown in this report were implemented using either the ImageJ macro language or the ImageJ Python scripting engine. Basic noise removal, Illumination correction and Segmentation are the basic of the imaging analysis.

In case of large area detector a set of picture will be taken and by stitching a large picture will be composed.

Roundness and endpoint thresholds can be adjusted to obtain fewer false negatives at the expense of more false positives. A receiver operation characteristic (ROC) can be used to characterise this.

The high and low threshold determination in the hysteresis thresholding step should be improved.

After the automated procedure the operator can go over the FT and decide if to add stars that were not found by the software or to cancel stars that are artifact.

Correlation between forensic and image processing parameters will be defined. Even that stars are coming from <sup>235</sup>U only and it is no one to one connected only to enrichment we still think that the shape, color, number of end points and roundness can be parameters to indicate different forensic properties.

9:00am **AC+AS+SA-TuM4 Application of Linear Least Squares to the Analysis of AES Depth Profiles of Plutonium Oxides, Scott Donald, A.J. Nelson, Lawrence Livermore National Laboratory**

Application of the linear least squares (LLS) methodology allows for quantitative determination of variation in material composition with depth, as well as permitting an understanding of differences resulting from changes in the method of preparation. LLS fits were applied to decompose and enhance the interpretation of spectra obtained by Auger electron spectroscopy (AES) during depth profiles of oxidized plutonium surfaces. By means of the LLS algorithm, chemical state assignments of the Pu P<sub>1VV</sub>/O<sub>45VV</sub>, O KLL, and C KLL Auger transitions were determined and the existence of a subsurface oxy-carbide layer was identified, with confirmation provided from comparison to previous measurements of standard samples.

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

9:20am **AC+AS+SA-TuM5 Physical and Chemical Characterization of Solid Pu and Np Sources after Multi-year Exposure to Environmental Conditions, Brian Powell, Clemson University** **INVITED**

A field scale radionuclide vadose zone transport experiment at the United States Department of Energy Savannah River Site is being operated by Savannah River National Laboratory and Clemson University scientists. In this experiment, plutonium and neptunium solid sources are buried in 61 cm long x 10 cm diameter lysimeters which are open to precipitation. Such experiments provide the opportunity to observe changes in the microcrystalline structure of plutonium and neptunium solid phases under various environmental conditions. In the current experiments, sources of neptunium and plutonium in multiple initial oxidation states and chemical forms have been deployed for 2-5 years of field exposure. These sources include Pu(V)NH<sub>4</sub>CO<sub>3</sub>(s), Pu(IV)(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(s), Pu(III)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(s), Pu(IV)O<sub>2</sub>(s), Np(IV)O<sub>2</sub>(s) and NpO<sub>2</sub>NO<sub>3</sub>(s). X-ray absorption spectroscopy (XAS) analysis of initially Pu(V)NH<sub>4</sub>(CO<sub>3</sub>) sources archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to Pu(IV) within the sources leading to the formation of Pu(IV)O<sub>2</sub>(s). Thus, there appears to be an auto-reduction of NH<sub>4</sub>Pu(V)CO<sub>3</sub>(s) to Pu(IV)O<sub>2</sub>(s) even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40% Pu(V) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(V). XAS and electron microscopy studies have demonstrated differences between Pu(IV)O<sub>2</sub>(s) formed via reduction of Pu(V)O<sub>2</sub>NH<sub>4</sub>CO<sub>3</sub> and initially Pu(IV)O<sub>2</sub> formed from precipitation of a Pu(IV) solution. The behavior of initially Np(IV)O<sub>2</sub> sources was quite different showing oxidation to Np(V) and subsequent downward transport of more soluble Np(V)O<sub>2</sub><sup>+</sup>. The oxidation of Np(IV)O<sub>2</sub>(s) leads to formation of a much more disordered solid phase with a significantly altered morphology than the initial Np(IV)O<sub>2</sub>(s). The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

11:00am **AC+AS+SA-TuM10 Synchrotron Radiation Investigation of f-element Extraction from a Carboxylic Acid Functionalized Porous Aromatic Framework, David Shuh, Lawrence Berkeley National Laboratory, S. Demir, N.K. Brune, University of California Berkeley, LBNL, J.F. Van Humbeck, J.A. Mason, University of California Berkeley, T.V. Plakhova, Lomonosov Moscow State University, Russia, S. Wang, University of California Berkeley, LBNL, G. Tian, S.G. Minasian, T. Tysliszczak, Lawrence Berkeley National Laboratory, T. Yaita, T. Kobayashi, Japan Atomic Energy Agency, S. Kalmykov, Lomonosov Moscow State University, Russia, H. Shiwaku, Japan Atomic Energy Agency, J.R. Long, University of California Berkeley**

Porous aromatic frameworks (PAFs) incorporating a high concentration of acid functional groups possess characteristics that are promising for use in separating lanthanide and actinide metal ions, as required in the treatment of radioactive waste. These materials have been shown to be indefinitely stable to concentrated acids and bases, potentially allowing for multiple

adsorption/stripping cycles. Additionally, the PAFs combine exceptional features from metal organic frameworks (MOFs) and inorganic/ activated carbons giving rise to tunable pore surfaces and maximum chemical stability. The adsorption of selected metal ions,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Am}^{3+}$ , from aqueous solutions employing a carbon-based PAF, BPP-7 (Berkeley Porous Polymer-7) has been investigated. This material displays high metal loading capacities together with excellent adsorption selectivity for neodymium over strontium. X-ray absorption spectroscopy studies show that the stronger adsorption of neodymium is attributed to multiple metal ion and binding site interactions resulting from the densely functionalized and highly interpenetrated structure of BPP-7. Recyclability and combustibility experiments demonstrate that multiple adsorption/stripping cycles can be completed with minimal degradation of the polymer adsorption capacity.

11:20am **AC+AS+SA-TuM11 The Effect of  $\text{Al}_2\text{O}_3$  Encapsulation Using Atomic Layer Deposition on the Photoluminescent, Water and Thermostability Properties of  $\text{SrAl}_2\text{O}_4$  Based Phosphors**, *Erkul Karacaoğlu, E. Öztürk*, Karamanoglu Mehmetbey University, Turkey, *M. Uyaner*, Selcuk University, Turkey

Aluminate based phosphors ( $\text{MAl}_2\text{O}_4$ ,  $\text{M}_4\text{Al}_{14}\text{O}_{25}$ , M= Sr, Ba, Ca, etc.) are chemically unstable against water and even moisture. Moreover, some of phosphors, like green emitting phosphorescent materials' luminescence properties, but not their structural properties, are affected negatively during reheating applications because the  $2+$  ionic state of europium is oxidized to  $3+$  in open atmosphere low temperature heating process thus limiting their applications. Their hydrolysis process were studied and analyzed intensively by researchers. Changes of pH value of suspensions, the structures and optical properties of the hydrolysis of phosphor structures had been investigated. In this research, to prevent or minimize this degradation, to enhance the water resistance and to maintain the phosphorescence properties, an  $\text{Al}_2\text{O}_3$  coating on the surface of  $\text{SrAl}_2\text{O}_4$  based phosphor pellets (1 mm thickness) were prepared using Atomic Layer Deposition (ALD) method with Trimethylaluminum (TMA) precursor. The investigation of phase formation of strontium aluminate was analyzed by thermal analysis (DTA/TG) until  $1500\text{ }^\circ\text{C}$ . The  $\text{SrAl}_2\text{O}_4$  with Monoclinic structure in single phase having lattice parameters  $a=8.44365\text{ \AA}$ ,  $b=8.82245\text{ \AA}$ ,  $c=5.15964\text{ \AA}$  and  $\alpha=90^\circ$   $\beta=90^\circ$   $\gamma=90^\circ$  were obtained according to XRD analysis. The photoluminescence (PL) results of both open and reduced atmosphere synthesized phosphors with excitation and emission wavelengths and decay time were determined by a PL spectrometer at room temperature. The reduced and open atmosphere synthesized samples have different photoluminescent characteristics because of ionic state of europium in  $2+$  and  $3+$  at reduced atmosphere and open atmosphere, respectively. Moreover, it was obtained that the main crystal,  $\text{SrAl}_2\text{O}_4$ , had photoluminescent properties. The surface analysis of phosphors as morphology and elemental analysis (SEM/EDX), X-ray diffraction (XRD), water and heat resistance (thermostability), photoluminescence (PL) of the phosphors before and after encapsulation were discussed in detail.

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