NUCL 1

Chromatographic separation of medically-related radionuclides from proton-irradiated thorium targets

Tara Mastren[1]*, tmastren@gmail.com, Valery Radchenko*[1]*, Jonathan W. Engle*[1]*, Allison Owens*[2]*, Roy Copping*[2]*, Mark Brugh*[1]*, F. M. Nortier*[1]*, Eva R. Birnbaum*[1]*, Keven D. John*[1]*, Michael E. Fassbender*[1]*. (1) Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Clinicians rely on nuclear medicine for the treatment of numerous diseases impacting millions of patients annually. Recently, targeted radiotherapy (TR) has been successfully advanced with the US FDA approval of several radionuclide-based drugs. One of the limiting factors in the development of TR as a widely adopted treatment option is the availability of select radionuclides with optimum emission properties, which poses a challenge due to the fact that different radionuclides typically require different target materials and/or nuclear reaction pathways for their formation. Proton-induced fission on heavy Z targets is one way to obtain multiple radionuclides from one target irradiation. Currently at Los Alamos National Laboratory, ^{225}Ac is produced from the proton irradiation of thorium targets. In this work, column chromatographic methods have been developed to separate the medically related fission product radionuclides ^{111}Ag, ^{223,224,225}Ra and ^{103}Ru as an ancillary processes to the existing ^{225}Ac recovery process. Separation of ^{111}Ag was achieved using CL resin, an extraction chromatography resin carrying alky phosphine sulfide groups. The recovery yield of ^{111}Ag was 93 ± 9 % with a radiochemical purity of 99.9% (prior) and 87 ± 9% with a radiochemical purity of 99.9% (subsequent to) ^{225}Ac recovery. The separation of ^{223,224,225}Ra from the thorium matrix was obtained with an overall recovery yield of 91 ± 3%, average radiochemical purity of 99.9%, using chelation/cation chromatography subsequent to ^{225}Ac recovery. Ruthenium-103 was isolated using an anion exchange column to remove ^{103}Ru prior to capturing ^{225}Ac on a cation column, followed by chelation chromatography to separate antimony contaminants. The overall recovery yield was ≥ 70 ± 5 % with an average radiochemical purity of 99.9%. These isotopes of interest were recovered from the irradiated thorium target with minimal impact to the ^{225}Ac process.

NUCL 2

Building a reference database for thermodynamic sorption modelling

***Frank Bok**, f.bok@hzdr.de, Anke Richter, Vinzenz Brendler. Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf e.V., Dresden, Germany*

Any safety assessment of waste disposal concepts requires comprehensive and consistent thermodynamic data for the respective reactive transport modelling. This includes sorption, ion exchange or surface precipitation as major retardation processes. The current lack of respective quality-assured databases for these interface phenomena (invalid reaction formulation, missing consistency, restricted application ranges, and contradictory data) severely hampers a reliable modelling.

This work aims on a re-evaluation of already published sorption raw data based on spectroscopically verified surface complexes and their formation reactions. This shall help to transform the free-for-use digitized sorption data collection RES^{3}T (http://www.hzdr.de/res3t) into a true thermodynamic reference database be used for complex real systems such as rocks or soils following the “Component Additivity” approach. Coupled to this is an extension of RES^{3}T allowing also for the storage of sorption raw data sets. Eventually, a full integration with the thermodynamic reference database THEREDA (http://www.thereda.de) is envisaged to provide a comprehensive database for a holistic geochemical modeling.

Sorption speciation calculations of radionuclides on various mineral surfaces will be presented, showing the actual consequences of inconsistent sorption data that can be found in literature, as well as the possibilities using a validated surface speciation. The latter is mainly based on a combination of ATR FT-IR, TRLFS, and EXAFS which allows to create chemically realistic surface complexing models. In combination with the site-density data (including ones from crystallographic measurements), surface complexation models are deduced that describe the sorption of radionuclides accurately and with less surface species then assumed in a vast number of literature references published in the past. Due to the correct description of the realistic surface chemistry and the internal consistency, these models are more robust to other chemical and environmental conditions (pH, pe, composition of the aqueous phase).

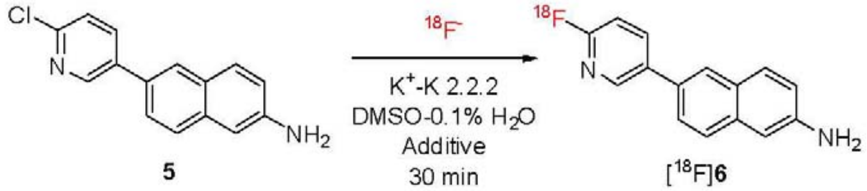
As examples, the sorption of uranium(VI) onto various mineral phases (Al-, Fe- and Si-phases), ubiquitous in nature will be presented.

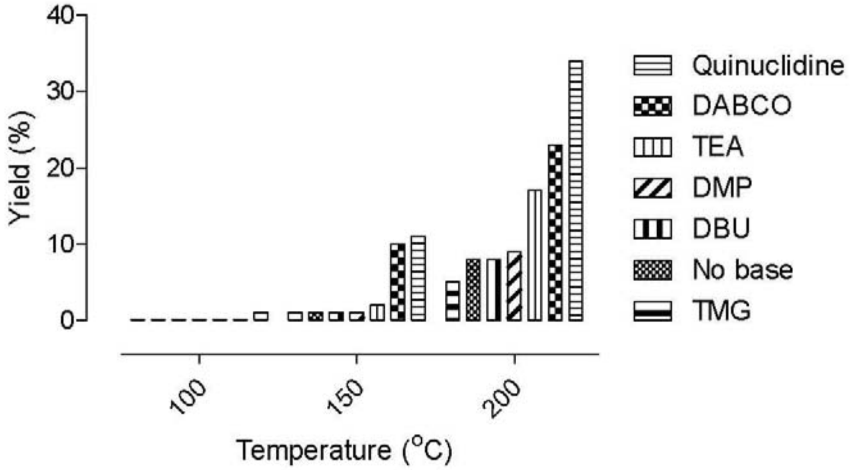
NUCL 3

Dabco/quinuclidine increases the radiofluorinations of 2-halopyridines

Lisheng Cai[1], *cail@intra.nimh.nih.gov, Gregory R. Naumiec*[2], *Shuiyu Lu*[1], *Victor W. Pike*[1]. *(1) PET Chemistry/MIB, National Institute of Mental Health, Bethesda, Maryland, United States (2) Department of Chemistry and Biochemistry, University of Central Arkansas, Conway, Arkansas, United States*

Many interesting PET radioligands contain fluoro-pyridine moiety, such as [^{18}F]AZD4694 for Aβ-amyloid in Alzheimer's disease, [^{18}F]T807 for neurofibrillary tangle in Alzheimer's disease, [^{18}F]NCFHEB for α4β2-nicotinic acetyl choline receptors (nACnRs), [^{18}F]fluoroisonicotinamide for melanoma cancer, and many other radioligands. A variety of synthetic radiolabeling methods have been developed to synthesize these radioligands, with different leaving groups, such as halide, tosylate, -NO_2, and –NR_3^+. Not every precursor is synthetically available, since these with the most reactive leaving groups are normally much challenge to synthesize. There is a need for auxiliary agents to activate somewhat inert precursor for radiolabeling by [^{18}F]fluoride. We have developed a group of additives based on dabco/quinuclidine, and their other analogs, to facilitate the radiolabeling of fluoro-pyridine moiety by [^{18}F]fluoride. The scope and limitation of this radiolabeling method are described here.





NUCL 4

Accumulation of specific radioisotopes by fish in offshore Fukushima, Japan

Hidemitsu Katsura[1,2]*, hi@katsura.dk. (1) IPROM, Uni KL, Chigasaki-Shi, Japan (2) ICEEE-2016, Coimbatore Institute of Technology, Coimbatore, Tamil Nadu, India*

The Tokyo Electric Power Company's, Fukushima Dai-ichi nuclear power plant in Fukushima-Ken (Fukushima Prefecture), Japan, was destroyed in March 2011 by a massive magnitude 9 earthquake (centred offshore to the northeast of Honshu Island) and by the subsequent historic tsunami of March 11, 2011. Because of the nuclear meltdown, hydrogen-explosion damage to the buildings that housed the reactors, and the contamination of the cooling water from the reactor cores, large quantities of radioisotopes were emitted into the atmosphere and adjacent seawater. Fishing is currently restricted off the coast of Fukushima-Ken because intermittent surveys have found part of the fishery products still contain high levels of radioisotopes. The Tokyo University of Marine Science and Technology has measured radioisotope levels in fishery species off Iwaki-Shi(Iwaki City), Fukushima-Ken(located south of the former nuclear power plant); these data could be used to understand the relationship between the accumulation of specific nuclides (radioisotopes) and certain species of fish, as follows:

#1 The Total Fish Weight % of ***Okamejei kenojei*** spp. and ***Sebastes cheni*** in this sampling in offshore Fukushima-ken,Japan were 26.6824 Weight% and 13.700005 Weight%, respectively; additionally, the fish bodies of ***Okamejei kenojei*** spp. and ***Sebastes cheni*** had 49.322578 becquerel% and 33.037159 becquerel% of 134Cs, respectively, and had 50.479187becquerel% and 31.779293 becquerel% of 137Cs, respectively. Therefore, ***Okamejei kenojei*** spp. has ability to accumulate 1.8485 times of their weight % for 134Cs and 1.92168 times of their weight% for 137Cs. However, ***Sebastes cheni*** has the ability to accumulate 2.411 times of their weight% for 134Cs and 2.3195 times of their weight% for 137Cs.
#2 It is possible to accumulate or separate specific nuclides (134Cs and 137Cs) by combining ***Sebastes cheni*** and ***Kareius bicoloratus***, and ***Ditrema temmincki temmincki*** and ***Cynoglossus joyneri***.

#3 There are differences in 134Cs and 137Cs accumulation between adult fish and fry of ***Paralichthys olivaceus***.

Therefore, some fish species have the ability to accumulate a specific nuclide (radioisotope). To date, ultra-centrifugation and diffusion methods have been used to accumulate specific nuclides for atomic fuel. However, if we could use the ability of some fish species to accumulate specific nuclides, we would have additional methods to concentrate nuclides.

NUCL 5

Cesium ion partitioning with ionophores in ionic liquid-water biphasic systems

***Rima Biswas**[1], biswasrima622@gmail.com, Tamal Banerjee[2], Pallab Ghosh[2], Sk. Musharaf Ali[3]. (1) Chemical Engineering, IIT Guwahati, Guwahati, Assam, India (2) Dept of Chemical Engineering, Indian Inst of Tech Guwahati, Assam, India (3) Chemical Engineering Division, Bhabha Atomic Research Center, Mumbai, Maharashtra, India*

Cesium is an extensive fission product in spent nuclear fuels. The removal from the nuclear wastes forms a key part of waste remediation strategies. We report the molecular dynamics studies on the interfacial behavior of cesium (Cs^+) extraction by bis(2-propyloxy)calix[4]crown-6 (BPC6) and dicyclohexano-18-crown-6 (DCH18C6). For the benchmarking study, the phase separation for [BMIM][Tf_2N]-water was validated. Thereafter, to understand the mechanism of complexation and the behavior of crown ether ligand, crown ether (CE) molecules and $Cs^+NO_3^-$ ions were inserted randomly in the ionic liquid (IL) water biphasic system. It was observed that the Cs^+-CE complex formed during the simulation diffused at a slow rate as compared to other free species from the interface to the bulk IL phase. The radial distribution function (RDF), interaction energies and the diffusion coefficient during complexation of Cs^+ cation with BPC6 and DCH18C6 crown ether were also computed. Within the limited sample size of twelve crown ethers and six cesium nitrate molecules, BPC6 and DCH18C6 were able to capture two and one cesium atom(s) respectively towards its crown cavity after a 40 ns simulation time. In case of BPC6 the captured cesium atoms were found to lie towards the IL part of the interface. This work hence summarizes the interface phenomena.

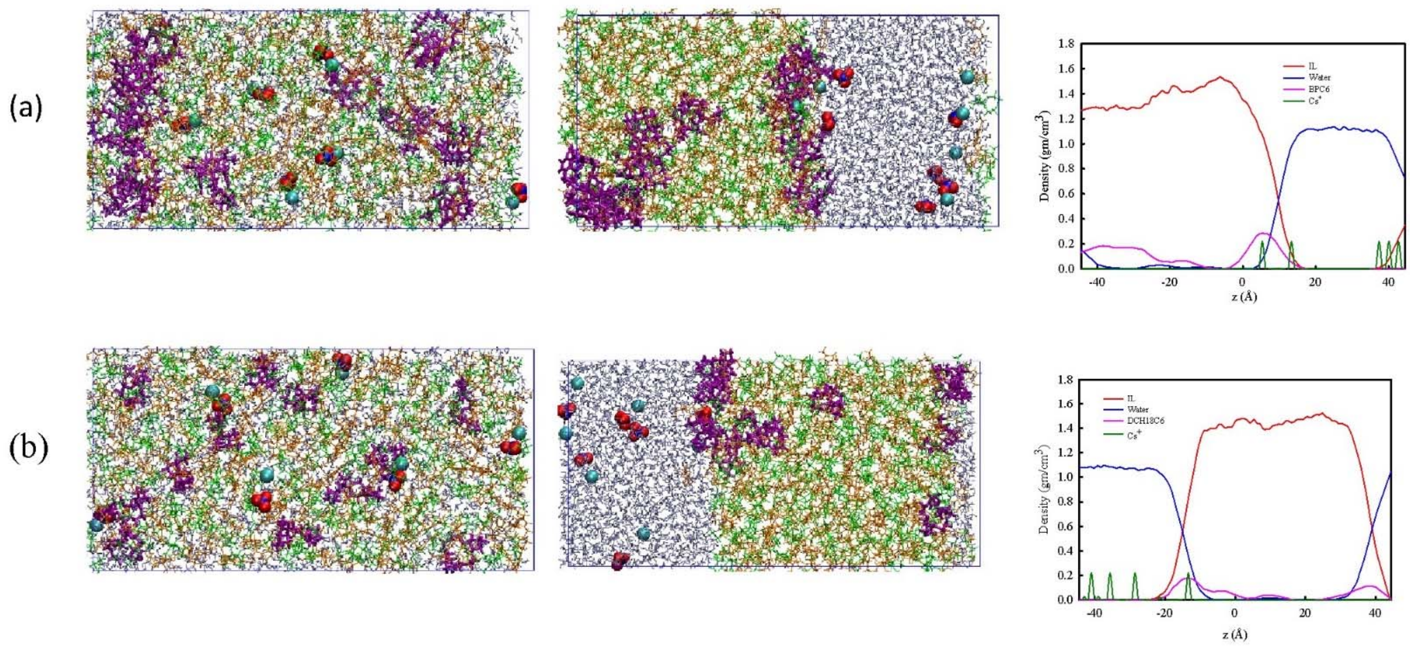


Figure 1. Initial and Final snapshots of demixing IL-water systems with (a) BPC6 and (b) DCH18C6. Plots for density are affixed to the right side.

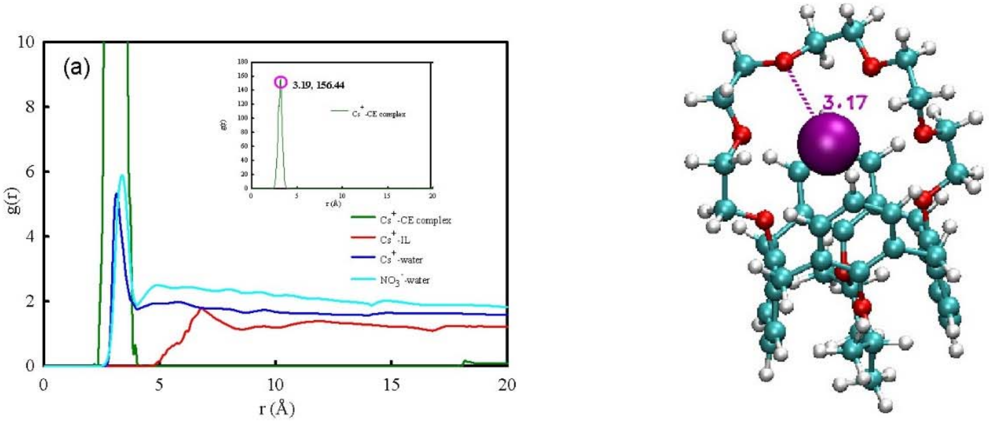


Figure 3. Optimized geometry of Cs^+–BPC6 complex. (a) RDF for Cs^+-O complex over the trajectory run from 30 to 40 ns. (b) Equilibrium distance between Cs^+ (purple) and O of BPC6 (red) is shown by purple dotted line.

NUCL 6

Change of electronic structure in U-10Zr metallic fuel from high-temperature annealing

Young-Sang Youn[1], *ysyoun@kaeri.re.kr, Jeongmook Lee*[1], *Jong Hwan Kim*[2], *Hoon Song*[2], *Jeong-Yong Park*[2], *Jong-Yun Kim*[1,3]. *(1) Nuclear Chemistry*

Research Division, Korea Atomic Energy Research Institute, Daejeon, Korea (the Republic of) (2) Next Generation Fuel Development Division, Korea Atomic Energy Research Institute, Daejeon, Korea (the Republic of) (3) Radiochemistry & Nuclear Nonproliferation, University of Science & Technology, Daejeon, Korea (the Republic of)

The electronic configurations of U-10wt %Zr (U-10Zr) metallic fuel before and after annealing at 610°C were studied by observing three core-level spectra (U 4f, Zr 3d and C 1s) using X-ray Photoelectron Spectroscopy (XPS). We found that the surface of U-10Zr metallic fuel under ambient conditions was spontaneously oxidized into hyperstoichiometric UO_{2+x} and Zr_2O_3 with a small amount of uranium metal. After annealing at 610°C, it was composed of uranium metal, uranium carbide, uranium oxide, and zirconium metal. Raman results indicate that no distinct peaks were observed in U-10Zr metallic fuel at room temperature, whereas amorphous carbon (α-C) occurred after annealing at 610°C. X-ray diffraction (XRD) data show that the bulk composition of U-10Zr metallic fuel from annealing was preserved with only slight variations in the lattice parameters. In conclusion, the original U-10Zr surface contained UO_{2+x}, Zr_2O_3, a low amount of uranium metal, whereas it consisted of uranium metal, uranium carbide, uranium oxide, zirconium metal, and α-C after annealing at 610 °C. We predict that research on the variations in the composition in U-10Zr metallic fuel will contribute to an improvement in knowledge regarding metallic fuels.

NUCL 7

Progress towards online isotope harvesting at the NSCL

Gregory Severin[5], *gwseverin@chemistry.msu.edu, Suzanne Lapi*[4], *John D. Robertson*[3], *Graham F. Peaslee*[2], *David J. Morrissey*[1]. *(1) Dept. of Chemistry, Michigan State University, East Lansing, Michigan, United States (2) Notre Dame University, South Bend, Indiana, United States (3) Univ of Missouri, Columbia, Missouri, United States (4) University of Alabama Birmingham, Birmingham, Alabama, United States (5) Michigan State University, East Lansing, Michigan, United States*

Heavy-ion fragmentation at the National Superconducting Cyclotron Lab (NSCL) creates an abundance of useful radionuclides. Since the facility is specifically designed to deliver one exotic-nuclear species at a time to nuclear physics experiments, the remainder of the radionuclides are unused and are left to decay. Our purpose is to take advantage of these unutilized reaction products by desigining chemical "harvesting" and purification systems that will

allow them to be extracted as a part of normal NSCL operation. Already-proof-of-principle harvesting has been demonstrated with ^{24}Na, ^{67}Cu, ^{85}Kr, and ^{48}V in dedicated experiments. The next step is to operate the harvesting equipment while the primary nuclear physics experiments are running. This requires a new water-cooled beamstop, where unused radionuclides will be collected and transported to purification systems-- like ion exchange resin beds and membrane contactors. The design of the beam-stop and the purification systems will be presented, along with plans for purifying the mixed stream of products, and potential uses.

NUCL 8

Nitric and sulfuric acid mixture pressure decomposition of graphite probes used in nuclear fusion research

Seungsup Lee[1]*, slee148@vols.utk.edu, Lauren Finney*[2]*, Jonah Duran*[1]*, Shawn Zamperini*[1]*, Jack Nowotarski*[1]*, Anurag Maan*[1]*, Christopher Eley*[1]*, John Auxier*[1]*, David Donovan*[1]*. (1) Nuclear Engineering, University of Tennessee - Knoxville, Knoxville, Tennessee, United States (2) Chemistry, University of Tennessee - Knoxville, Knoxville, Tennessee, United States*

An improved graphite dissolution method has been identified utilizing nitric and sulfuric acid mixtures and a pressurized microwave digestion system, for which dissolution temperature, pressure, and time were varied to find the ideal settings. Graphite probes are inserted into the edge of nuclear fusion experiments to collect impurities in the fusion plasma. Impurities can cause prohibitively elevated levels of radiative power loss in plasmas, which could hinder the performance of nuclear fusion as a net energy source. For this reason, it is important to measure the precise concentration of impurities collected by the graphite probes to better understand impurity transport in a fusion device. However, conventional nitric acid digestion of graphite leaves visible amounts of graphite particles, which cause graphite matrix effects when using inductively coupled plasma mass spectrometry (ICP-MS). To remove this effect, graphite powder samples were decomposed with a mixture of 2 ml of nitric acid and 2 ml of sulfuric acid using a pressurized microwave digestion system. Heated dissolution in atmosphere using a hot plate was compared but due to excessive nitric acid evaporation, it was unsuccessful. Various temperatures and pressures were investigated to find an optimal condition. The result showed that the higher the temperature (up to 240 degree Celcius), the better the decomposition. Intermediate pressure (150 psi) displayed the best result due to less nitric acid evaporation and more reaction product gas release. These optimal conditions were then used to determine

the maximum amount of graphite possible for decomposition. Three types of graphite commonly used in fusion plasma experiments were investigated (ATJ, Ted Pella Spectroscopically Pure, and Sigrafine). A clear solution (no visible graphite remaining) was confirmed as a preliminary result by visually comparing before and after the decomposition process. Residual carbon content determination will be used as a measurement of completeness of decomposition. This presentation will discuss the nitric and sulfuric acid mixture pressurized microwave decomposition method of graphite developed for better ICP-MS analysis of impurities collected by graphite collector probes used in nuclear fusion experiments.

NUCL 9

Analysis of γ-ray emitting radionuclides in food matrices using cerium bromide γ-ray spectrometry

Thomas Scott, *tomscott75@yahoo.com, Cong Wei, Kelly Garnick, Jennifer Szymanski, Elon Malkin. ORA/WEAC, US Food and Drug Administration, Winchester, Massachusetts, United States*

Gamma spectroscopy is a useful relatively non-destructive qualitative or quantitative method for radioactivity analysis. Sodium Iodide (NaI) scintillation or high purity germanium (HPGe) detectors are the types most commonly utilized. Scintillators are widely used because of their high light yield, high efficiency, response speed, linear response, limited maintenance, and low cost. The main deficiency of this type of detector is the poor resolution when compared to HPGe detectors. The recently developed Cerium Bromide (CeBr) scintillation detectors provide better resolution than traditional NaI detectors without the cooling requirements of HPGe detectors.

Gamma spectrometers are a primary tool for screening and testing food supplies for potential radioactive contamination. When considering measurements of food matrices, one of the main considerations is the density of the food which has a direct impact on the attenuation of photons. Density corrections have traditionally been addressed through measuring a series of radioactive calibration standards with varying density and creating a detector specific attenuation curve. Advances in Monte Carlo based efficiency calculations can be utilized to correct for density without the need for a series of expensive calibration standards.

In this work, we investigate the detection and quantification capabilities of

portable CeBr scintillation detectors to assay food matrices of different densities using calculated efficiencies.

NUCL 10

Investigation of covalency in the transuranic elements under non-aqueous conditions

***Shane Galley**, shanesteven182@gmail.com. Florida State University, Tallahassee, Florida, United States*

Most coordination chemistry that has been studied with the actinide series has only utilized ligands stable to oxygen and moisture due to the scarcity and radiation hazards associated with these elements. Additionally, the non-aqueous chemistry of the transuranic elements is relatively unexplored and offers a wider platform for exploring methods of deducing electronic structure and information about the actinide-ligand bond. Such information can be very useful for discovering trends in the whole series. In the reported work, a series (Th-Cf) of complexes using the redox active ligand 2,4,6,8-tetrakis(tert-butyl)-9-hydroxyphenoxanone (HDOPO) were synthesized in non-aqueous conditions under an inert atmosphere and have been fully characterized with the help of X-ray, optical, magnetic, and computational techniques. Crystallographic data reveal An(DOPO)3 complexes, yet U, Np, and Pu are clearly not in the same oxidation state as Am(III) and Cf(III). Furthermore, the Cf(III) complex disrupts the tris-chelate trend due to radiolysis. It is also shown that the ligand undergoes redox transitions to stabilize the higher oxidation states of the earlier actinides. The results will help contribute toward gaining foundational knowledge of structure and bonding in non-aqueous transuranic chemistry as well as give insight into the participation of f-orbitals in bonding.

NUCL 11

New chemical media for superheavy element study

***Evgeny Tereshatov**[1], etereshatov@tamu.edu, Maria Boltoeva[2,3], Merinda Volia[1], Charles M. Folden[1]. (1) Cyclotron Institute, Texas A&M University, College Station, Texas, United States (2) Université de Strasbourg, IPHC, Strasbourg, France (3) CNRS, Strasbourg, France*

Recently, new chemical systems such as room temperature ionic liquids, deep eutectic and low-transition-temperature mixtures are of major interest for studying a variety of chemical processes, including, for example, liquid-liquid

extraction. Based on this new class of compounds, we have focused our efforts on development of a unique chemical procedure that might be applicable for superheavy element investigation. Homologs of element 113, nihonium, were chosen for such experiments. Results on indium and thallium behavior in these new chemical media will be presented.

The latest generation of fluorinated ionic liquids is widely used for metal extraction mostly as a safe replacement of conventional solvents. However, it was found that pure ionic liquids may be both suitable in this process and possess the required selectivity. It was shown that pure ionic liquids can provide a separation factor of 10^8 between indium and thallium when the latter is oxidized to its +3 state. Different parameters such as aqueous phase acidity, oxidizing agent, ionic liquid structure and extraction kinetics were systematically investigated.

The newest generation of deep eutectic and low-transition-temperature mixtures is also attractive for other applications, despite that these mixtures are mostly hydrophilic. However, hydrophobic mixtures are also available and the first results on metal transfer into these media will be presented. It was shown that tetraalkylammonium-based mixtures can provide a distribution ratio of indium at a level of $>10^3$. The influence of hydrogen bond donor and acceptor (the main structural units of such mixtures) was also studied.

Also, a mathematical model to describe indium and thallium behavior was developed for the chemical systems mentioned above to provide understanding of the extraction mechanisms. In both cases, it was shown that ion pair formation prevails, and the corresponding constants were estimated.

To provide a knowledge transfer between ordinary liquid-liquid extraction and gas phase chemistry, new surfaces are being examined to optimize conditions for online experiments. These preliminary results will also be discussed.

NUCL 12

Initial attempts into characterizing surrogate nuclear fireballs with UV-Vis spectroscopy

John D. Auxier[1,2]*, jdauxier2@yahoo.com, Cody Nizinski*[1,2]*, Eric J. Francis*[1,2]*, B L. Magocs*[1,2]*, Howard Hall*[3,1]*. (1) Department of Nuclear Engineering, Institute for Nuclear Security, Jefferson City, Tennessee, United States (2) Radiochemistry Center of Excellence, University of Tennessee, Knoxville, Knoxville, Tennessee, United States*

In the immediate seconds after the detonation of a nuclear weapon a large plasma cloud is formed. This plasma cloud has a unique environment due to the pressure and temperatures that are achieved. To simulate the high temperature efforts, collaborations between Oak Ridge National Laboratory have been leveraged to setup an industrial grade plasma torch. This work will leverage the existing collaboration and laboratory facilities to investigate the plasma chemistry in real time to determine what processes of formation (e.g. oxide, nitride, sulfide, etc.) occur in different regions of the plasma (e.g. edge, center, etc.) using chemical compositions for the fallout recipes derived using the methods developed previously. After particulate matter is formed in the plasma region, the experimental chamber is set up to collect samples for investigation by scanning electron microscopy (SEM) and other similar morphological and surface chemistry characterization techniques. This talk will detail the early measurements that have been made in the UV-Vis region with regard to detection of elemental species.

NUCL 13

Precise control of polyhydroxamate ligand topology for selective actinide coordination

***Kirstin Sockwell**, aksockwell@gmail.com, Modi Wetzler. Chemistry, Clemson University, Pendleton, South Carolina, United States*

The similar charge/ionic radius ratios of iron(III) and plutonium(IV) allow for the utilization of strong iron chelators for a basis of actinide ligand design. Ferrichrome, a tris-hydroxamate siderophore (biological ligand used primarily for iron uptake in bacteria), has been the inspiration the design of potent ligands for actinides.

We are interested in two topologies for polyhydroxamate ligands. First, although ferrichrome is a cyclic peptide, in 70 years of research encompassing hundreds of reported analogs, almost no peptide analogs of it have ever been made/studied leaving many basic questions unanswered. For example, why are the three chelating arms in ferrichrome adjacent instead of symmetrically distributed around the cyclic peptide hexamer? Can larger, cyclic octamers be made that would make better ligands for *f*-block metals? Although cyclization of peptides remains challenging, peptoids (*N*-substituted glycine oligomers), allow for a straightforward modular synthesis of close ferrichrome analogs which incorporate hydroxamate-containing residues into a cyclic backbone.

Second, EDTA is a powerful chelator but is marginally too small even for iron(III), leaving a coordinated water. A decadentate hydroxamate EDTA-analog that replaces all the carboxylates with hydroxamates may be even smaller for a lanthanide or actinide. In that case a larger homolog may function better, but at what length? We have synthesized several such ligands varying the side chain length (1-3 methylenes) and rigidity (with or without an aromatic spacer) and are characterizing their lanthanide and actinide complexes via potentiometric titrations.

NUCL 14

Actinide ion complexes react with small organic molecules in the gas-phase

Jiwen Jian[1], *jianjiwen2006@gmail.com, Teresa Eaton*[3], *John K. Gibson*[2]. *(1) Chemical Science Division, Lawrence Berkeley National Lab, Berkeley, California, United States (2) Lawrence Berkeley National Laboratory, Emeryville, California, United States (3) Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California, United States*

Gas-phase actinide ion-molecule reactionsplay an important role in elucidating the bonding of 6d and 5f orbitals/electrons and reactivity of actinide ion complexes.Gas-phase anion complexes$[AnO_2L_2X]^-$and $[AnL_4X]^-$(An = U, Np, Pu; L =*cyclo*-C_6F_5COO; X= F, Cl) and cation complexes$[AnO_2(OH)L']^+$ (An = U, Np, Pu; L' =organic ligand)are synthesized by collision induced dissociation or electrospray ionization, and their reactions are studied in a quadrupole ion trap mass spectrometer.Potential reagents for reactions with these ion include methanol (CH_3OH), acetic acid (CH_3COOH), diethylamine($C_4H_{11}N$), trimethylsilane ($C_3H_{10}Si$) and 1-propanethoil (n-C_3H_7SH). For reactions that do proceed, actinide halogen (An-X) or actinide oxygen (An-O) bonds break, while An-O, An-N, An-Si or An-S bondsare generated, revealing fundamental aspects of actinide chemistry. Quantum chemistry calculation elucidate reaction mechanisms, includingkinetic barriers, for the bimolecular reactions carried out under low-energy/low-pressure conditions.

NUCL 15

Design and efficient synthesis of a bifunctional octadentate ligand for immunoPET imaging with Zr-89

Mahmoud Abdalrahman, *mah326@wildcats.unh.edu. Chemistry, University of New Hampshire, Durham, New Hampshire, United States*

Positron Emission Tomography (PET) imaging with Zr-89 has been gaining a lot of interest because it allows for extended imaging of slow processes such

as slowly-accumulating pharmaceuticals or changes in tumor size. In particular, it is suited for imaging with large biomolecules such as antibodies and nano-particles. Desferrioxamine-B (DFO) has been often used as the ligand of choice for imaging with Zr-89, but it has been found to lack stability *in vivo* causing the radio-active Zr-89 to accumulate in the bone, which has harmful effects. The hexadentate DFO leaves two coordination sites on Zr-89 open, which has been related to the *in vivo* instability of the complex. Otherwise, few bifunctional ligands meeting the general requirement of eight-coordination and high stability with Zr(IV) are known, and some of those require an extended synthetic route. In this work, we report the design, efficient one-step synthesis and aqueous speciation of a bifunctional octadentate Zr(IV) ligand.

NUCL 16

Radioactive waste forms for the future

Rodney C. Ewing[1,2], *rewing1@stanford.edu. (1) Geological Sciences, Stanford University, Stanford, California, United States (2) Center for International Security & Cooperation, Stanford University, Stanford, California, United States*

Over the past thirty years, there has been a considerable amount of research on nuclear waste forms of all types: glass, crystalline ceramics, composite ceramics and spent fuel. I will briefly survey the history of waste form development and discuss new challenges for the future. One of the very unique aspects of waste form research is the need to develop a means of predicting materials behavior over hundreds of thousands of years. There are a number of approaches: experimental, computational and the use of natural systems that must converge in order to build confidence in these long-term predictions. More recently, there have been discussions of matching the waste form to the characteristics of the waste stream or of selecting waste forms whose durability is compatible with the geochemical and hydrologic conditions in a geologic repository. In both cases, the nuclear waste form adds value to the safety assessment of a geologic repository.

NUCL 17

Role of Np(V) solid phases in the solution chemistry of neptunium under alkaline pH conditions

Xavier Gaona[1]*, xavier.gaona@kit.edu, David Fellhauer*[1]*, Jun-Yeop Lee*[1]*, Katja Hinz*[1]*, Vladimir Petrov*[2]*, Mark A. Silver*[3]*, Donald T. Reed*[4]*, Thomas E. Albrecht-Schmitt*[3]*, Marcus Altmaier*[1]*, Horst Geckeis*[1]*. (1) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany (2) Lomonosov Moscow State University, Moscow, Russian Federation (3) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (4) Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

For the long-term safety assessment of nuclear waste repositories, a thorough understanding and thermodynamic description of the principal geochemical processes of actinides in aqueous solutions is highly relevant. Solubility phenomena strongly control the radionuclide source term, i.e. the maximum amount of dissolved radionuclide species potentially mobilized from a repository in the case of water intrusion. Due to its long half-life and abundance in spent fuel, ^{237}Np is of high relevance in this context. In aqueous solutions, Np(V) is thermodynamically stable over a wide range of E_h and pH conditions. According to the NEA–TDB thermodynamic selection, the solubility of Np(V) in dilute to concentrated NaCl–NaOH solutions is controlled by the binary phase NpO_2OH(am).
Very comprehensive solubility experiments with Np(V) in alkaline, dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions have been performed at KIT–INE, which reveal that the current chemical model for Np(V) needs to be extended. The formation of so far not considered ternary M–Np(V)–OH(s) phases with M = Na, Ca readily takes place under these conditions. Our experimental data show that the latter have significantly lower solubilities compared to NpO_2OH(am). A mild hydrothermal treatment of NpO_2OH(am) in NaCl and $CaCl_2$ solutions further promotes the formation of ternary M–Np(V)–OH(s) solid phases above $pH_m = 11$. No such ternary phases are observed under weakly alkaline pH conditions, although Np phases exposed to elevated temperature within this pH-range show also a decreased solubility compared to NpO_2OH(am). The presence of borate in NaCl and $MgCl_2$ solutions induces the transformation or NpO_2OH(am) into ternary Na/Mg–Np(V)–borate phases. These solid phases readily form at room temperature, and lead to a decrease of up 3 log-units in the solubility of Np(V) under weakly alkaline pH conditions. Although An(V) are normally considered as highly soluble and mobile, the results presented in this contribution show that sparingly soluble Np(V) solid phases can also form under boundary conditions relevant in the context of nuclear waste disposal. The combination of solubility experiments with extensive solid phase characterization allows the determination of thermodynamic models for the investigated systems. These models can be

implemented in thermodynamic databases and geochemical calculations, and thus represent a very useful tool in the safety assessment of repositories for nuclear waste disposal.

NUCL 18

Mystery of red technetium oxide

Keith V. Lawler[2], *keith.v.lawler@gmail.com, Bradley Childs*[2]*, Daniel S. Mast*[2]*, Kenneth Czerwinski*[2]*, Alfred P. Sattelberger*[1]*, Frederic Poineau*[2]*, Paul Forster*[2]*. (1) Rm A210, Argonne Nat Laboratory, Lemont, Illinois, United States (2) Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada, United States*

For decades it has been know that the oxidation of Tc (mainly from TcO_2) can result in a red oily, liquid compound. It was proposed that the red product was formed by the hydrolysis of Tc_2O_7 to $HTcO_4$ followed by the reduction of $HTcO_4$. We investigated several hydrated species of Tc_2O_7 and $HTcO_4$ with DFT/TD-DFT and show that these compounds do not exhibit the characteristic UV-Vis adsorption band around 510 nm. Electron-Ion mass spectrometry measurements of Tc_2O_7 indicated several other lower oxidation state candidate stoichiometries. We explored several molecular arrangements of these candidate stoichiometries, and have discovered a bonding motif that closely reproduces the experimentally observed adsorption at 510 nm. In addition, we explored dimer configurations that suggest why the red compound exists as an oily liquid and has not yet been crystallized.

NUCL 19

Probing the electronic structure and chemical bonding of d- and f-element compounds: A theoretical study of XAS spectra

Jing Su, *jingsu@lanl.gov, Maryline Ferrier, Justin N. Cross, Stosh A. Kozimor, Enrique R. Batista, Ping Yang. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Electronic structure and chemical bonding are the central theme of inorganic chemistry. X-ray absorption spectroscopy (XAS) has emerged as a powerful technique for characterizing electronic structure and covalent bonding. However, significant challenges remain interpreting the spectra of open-shell compounds with difficulties stemming from the large number of excited states involved in these spectra, appreciable multiplet effects, and the effect of spin-

orbit coupling (SOC). Density functional theory (DFT), which has a good balance between accuracy and computational cost, has emerged as an ideal approach for calculations of molecular electronic structures and spectra. In this work we will report DFT studies on the XAS spectra of transition metal, lanthanide and actinide compounds with open-shell ground states. The influence of the multiplet effects and SOC effects on the spectral shape and features will be discussed. Particularly, geometrical effects, which are usually neglected in previous reports, are found to be very important in reproducing the profile of the experimental spectra. Furthermore, the covalency of isoelectronic actinide/lanthanide-ligand bond will be compared and discussed.

NUCL 20

Au ion irradiation damage in glass-ceramics for immobilisation of waste actinides

Eric Vance, *erv@ansto.gov.au, Daniel Gregg, Tao Wei, Alan Xu, Yingjie Zhang, Inna Karatchevtseva. Austraiian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia*

Glass-ceramics containing mainly pyrochlore or zirconolite in borosilicate glass were made by sol-gel techniques followed by calcination in air and then hot isostatic pressing at 1200°C/100MPa/2h. These composites are candidate materials for the immobilisation of actinides, with some prepared using Ce as an actinide simulant. Waste actinides include U for example from spent fuel or PuO_2 and these ions are expected to partition to the ceramic phase. In contrast to the work on crystalline ceramics, little work has been published on the impact of accumulated radiation damage in glass-ceramics. Hence, we describe the results of 12 MeV Au ion damage at fluences of 10^{15}-10^{16} cm^2 which were studied by micro-Raman spectroscopy of cross-sections, scanning and transmission electron microscopy or glancing angle X-ray diffraction. Particular attention was given to how the glass matrix responds to the well-characterised anisotropic expansion in zirconolite which occurs with accumulated damage.

NUCL 21

Inorganic Ba-Sn composite materials for remediation of legacy nuclear waste contaminants

Isaac Johnson[2], *johnsonisaac16@yahoo.com, Sayandev Chatterjee[3], Gabriel B. Hall[3], Meghan Fujimoto[3], Tatiana G. Levitskaia[1]. (1) Battelle Pacif*

N West Natl Lab, Richland, Washington, United States (2) Energy and Environment, PNNL, Richland, Washington, United States (3) Pacific Northwest National Laboratory, Richland, Washington, United States

Sulfate is a difficult to remediate contaminant in Hanford tank waste. The presence of sulfate in the low activity waste (LAW) glass melt inhibits melter efficiency, interferes with retention of technetium-99 (Tc) in the glass matrix, and causes corrosion in the melter. In order to address these issues, as well as increase sulfate and Tc retention in the LAW glass, this research focused on development of a dual-functional material that could sequester sulfate in the LAW feed and reduce Tc(VII) to Tc(IV) prior to vitrification. Barium based composites were chosen because they can sequester sulfate, forming chemically and thermally stable barium and sulfate containing phases that are compatible with borosilicate glass. Tin(II) serves as a reductant for Tc(VII) which is poorly retained in LAW glass. The produced Tc(IV) is significantly less volatile at melter temperatures. A library of Ba-Sn composites has been developed and experimental results from optical spectroscopy, XRD, SEM/EDS, as well as other characterization techniques were obtained for the composites. It was observed that the ability of these materials to sequester sulfate and reduce Tc(VII) is highly dependent on solution pH during their preparation which in turn affects the structure of the formed phases. Composite performance was tested using simulated tank waste solution, and their impact on Tc retention in representative glass crucible tests was determined.

NUCL 22

Metal flux growth of uranium intermetallics

*Wes Potter, Thomas E. Albrecht-Schmitt, **Susan E. Latturner**, latturne@chem.fsu.edu. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

We are exploring the synthesis of complex uranium intermetallics from reactions in a variety of metal fluxes. Uranium silicides, aluminides, and borides are possible refractory waste forms, and may also exhibit unusual electronic properties such as heavy fermion behavior and superconductivity. Reactions of uranium and silicon in aluminum melts have yielded a new stuffed superstructure of the cubic UAl_3 structure type. $U_{32}Al_{76}Si_{24}$ crystallizes in the cubic Pm-3n space group with a = 16.8052Å. The occupancy of two stuffed interstitial sites in the structure yields the $U(Al_xSi_{1-x})_{3.125}$ stoichiometry. We will also report on results of reactions of refractory elements (B, Si, C) in

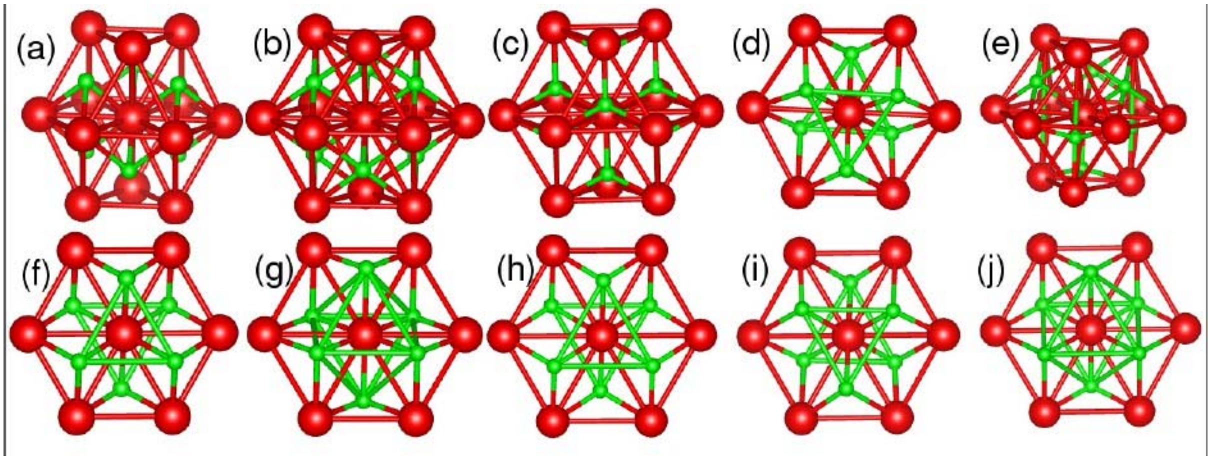
eutectic flux mixtures such as uranium and cobalt (63% U / 37% Co, mp 734 °C).

NUCL 23

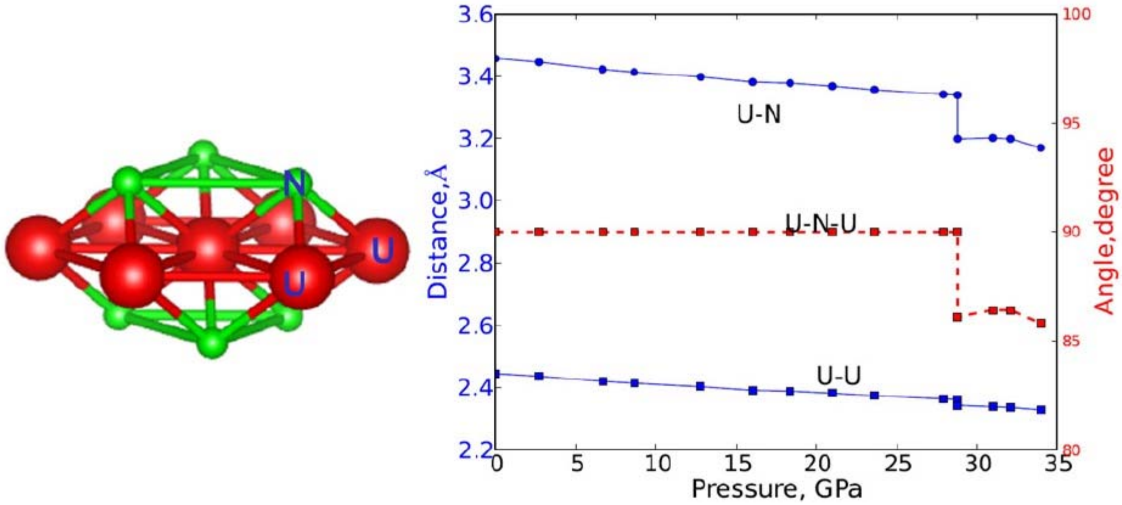
Insights into the phase relations in the U-N system using cluster formula

***Xin Wang**, wangxin@alum.imr.ac.cn. Institute of Materials, CAEP, Jiangyou, Sichuan, China*

Despite five kinds of uranium nitrides, i.e. uranium mononitrides (UN,R3m,Fm3m), uranium dinitride (UN2,Fm-3m), and uranium sesquinitrides (α-U2N3,Ia-3;β-U2N3,P-3m1), have been confirmed, until now the phase relations are not well understood due to the puzzling nonstoichiometric issue. This work reinvestigated the crystallographic structures of these phases using cluster formula theory. The principal clusters (cuboctahedron with six squares and eight triangles) in these phases were determined. N atoms can occupy either six octahedral sites (square face centers) or eight tetrahedral sites (formed by center atom and triangle) in the principal cluster of thirteen U atoms, resulting in these diversified phases and the nonstoichiometric issue. Also, the phase transformations at certain temperature and pressure: from CaF2-type UN2 to Mn2O3-type U2N3, from Mn2O3-type U2N3 to NaCl-type UN and from NaCl-type UN to HgIn-type UN, were deduced by tracking bonds and angle changes of a simplified cluster [U-U6N6]. This investigation provides an in-depth understanding of the phase relations in U-N system.



Clusters in these uranium nitrides. Up panel: The clusters formed by U atoms (CN12). (a) R-3m UN (b) Fm-3m UN, (c) Fm-3m UN2, (d) α-U2N3. (e) β-U2N3.
Bottom panel: The clusters formed by U and N atoms (CN12).(f) R-3m-type UN (g) Fm-}m$ UN, (h) Fm-3m UN2, (i) α-U2N3. (j) β-U2N3.



Bonds (U-N,U-U) and angle changes (U-N-U) as a function of pressure from Fm-3m UN to R-3m UN. The bonds and angles are indicated in the left panel.

NUCL 24

Salt-inclusion materials: A potential novel hierarchical wasteform

Hans Conrad zur Loye*, zurloye@mailbox.sc.edu. University of South Carolina, Columbia, South Carolina, United States*

A practical working definition of a hierarchical structure is that of a structural motif contained within a larger structure or framework. Salt Inclusion Materials (SIMs) are a subset of a unique family of crystalline hierarchical structure types that consist of a more covalent metal oxide framework containing voids filled by an ionic salt lattice. SIMs are noteworthy because as a “stuffed” porous material, this type of hierarchical material is of fundamental interest in the development of new waste forms for nuclear waste storage. These materials are of the general formula $[A_mB_nX][(UO_2)_p(M_qO_r)_t]$ where $[(UO_2)_p(Si_qO_r)_t]$ is the framework consisting of uranyl, UO_2^{2+}, and Si_qO_r units, where B_nX is the salt-inclusion and A are alkali or alkaline earth cations that are not part of the salt-inclusion. The presentation will focus on the synthesis, crystal growth, structures, and potential use of SIMs, including $[Cs_3F][(UO_2)(Si_4O_{10})]$, $[Cs_2Cs_5F][(UO_2)_2(Si_6O_{17})]$, $[Cs_9Cs_6Cl][(UO_2)_7(Si_6O_{17})_2(Si_4O_{12})]$, and $[Cs_2Cs_5F][(UO_2)_3(Si_2O_7)_2]$, with special emphasis on the overall crystal chemistry of these phases.

NUCL 25

New gas electrode for molten salt electrochemistry with metal-free, corrosion-resistance and real-time monitoring properties

***Guoyu Wei**, xjtuguoyu@qq.com. Tsinghua University, Beijing, China*

For molten salt electrolysis, where usually solid electrode such as noble metal and graphite acting as electrode couple, its application needs improvement especially in terms of electrode because of high cost and environmental pressure. The recent development of non-thermal microplasma electrode-atmospheric pressure micro-hollow direct current gas glow discharge electrode (GDE), benefitting from its characteristics of no-touching-electrolyte discharge and also serving as excitation source for optical emission spectrometry, could provide a multi-property alternative for molten salt electrolysis. In this paper, choosing Ag/Ag^+ redox couple as research object, we report the evidences of GDE performing as cathode and anode respectively to initiate charge-transfer reactions, and for first time present the evidences of GDE motivating Ag cations in molten salt to emit atom emission spectrum in order to monitor the element concentrate in melts. The results show that metal Ag ions could be electro-deposited to nanoparticles with above 90% current efficiency, and Ag ions concentration change during the process could be real-time monitored, testifying the feasibility that GDE could work as a metal-free, corrosion-resistance electrode with real-time monitoring function. The simplicity and real-time monitor properties of GDE compared to conventional solid electrode should lead to a new direction for molten salt electrochemistry.

NUCL 26

Tips and tricks for solid state assembly of actinyl cations

***Christopher L. Cahill**[1], cahill@gwu.edu, Robert Surbella[2], Korey Carter[2]. (1) George Washington Univ, Washington, District of Columbia, United States (2) The George Washington University, Washington, District of Columbia, United States*

Assembly of actinyl cations, $[AnO_2]^{2+}$, (where An = U(VI), Np(VI) and Pu(VI)) into desired, crystalline architectures is of broad interest owing to the relevance to spent nuclear fuel stewardship, waste forms, separations and environmental transport. Our efforts have historically focused on the use of carboxylate and phosphonate based ligands to generate $[AnO_2]^{2+}$ based

hybrid materials of higher structural dimensionality. More recently, however, we have focused on *molecular* materials wherein $[AnO_2]^{2+}$ species feature fixed first coordination spheres, and are in turn assembled through non-covalent interactions provided by judiciously placed synthons in (for example) the second coordination sphere. Presented will be an overview of two distinct approaches- the first features room temperature assembly in aqueous, high-anion media to generate $[AnO_2X_4(H_2O)_m]^{n-}$ (X = Cl, Br, NCS; m = 0,1; n = 2,3) anions, followed by assembly via hydrogen and halogen bond donating organic cations. The second utilizes chelating ligands (e.g. terpyridine, phenanthroline) under hydrothermal conditions to 'cap' the first coordination sphere, which not only prevents hydrolysis, but also allows for introduction of ligands functionalized for non-covalent interactions. Assembly proceeds as above, yet with additional opportunities to engage the nominally terminal 'O_{yl}' oxygen atoms via halogen-based interactions.

NUCL 27

Improvements in the licensing system for nuclear fuel cycle facilities in Korea

Hyeong Ki Shin[1], *hkshin@kins.re.kr, Seung Jae Han*[1], *Sang Hoon Park*[2]. *(1) Radiation Safety Research, Korea Institute of Nuclear Safety, Daejeon, Korea (the Republic of) (2) Radworks, Daejeon, Korea (the Republic of)*

As the cumulative capacity for storage of the spent fuel generated from operating nuclear reactors in Korea is expected to be gradually saturated in the near future, the Korean government announced a basic plan for high-level radioactive waste management. This includes the provision that spent fuel stored in NPPs shall be transferred to an interim storage facility before the on-site storage capacity is exceeded, and that a waste disposal facility shall be constructed and operated.

Because there are difficulties associated with securing the budget and the site when directly disposing of the spent fuel generated from light water reactors, there are on-going discussions in parallel, on how to utilize the spent fuel as a useful resource by recycling it, as an alternative to its direct disposal. For this purpose, pyro-processing (one of the dry methods for processing spent nuclear fuel) has been studied for years by researchers at the Korea Atomic Energy Research Institute (KAERI). However, there is no experience of safety review to license a spent fuel recycling facility in Korea yet, nor have its safety evaluation methods been established. Therefore, it would be necessary to review and prepare in phases, an improved licensing system for spent fuel processing facilities under the current Nuclear Safety Act in Korea.

In 2014, an IAEA Integrated Regulatory Review Service (IRRS) of the nuclear fuel cycle facilities in Korea, required that legal bases for the periodic safety review (PSR) and for the safety assessment report for an integrated safety assessment (ISA), including chemical and radiological hazards, should be provided to improve the safety regulatory framework of nuclear fuel recycling facilities.
In this study, a review of the licensing system for spent fuel recycling facilities under the Nuclear Safety Act was performed and compared with those of other nuclear facilities. Clauses in the Nuclear Safety Act in Korea, such as the legal basis for such facilities, the license application documents to be submitted, and the licensing steps, were reviewed with reference to IAEA Safety Standards and US regulatory documents, and some improvements were proposed. It is expected that the proposed improvements will be effectively utilized when revising the licensing system of the Korean nuclear fuel recycling facilities in the future.

NUCL 28

Investigation of Ln(III), An(III), and UO_2^+ binding properties of soft N- and S- donor site ligands

Ingrid Lehman-Andino[1], Megan Twomey[1,2], Logesh Mathivathanan[1], Raphael G. Raptis[1], Teresa Eaton[3], John K. Gibson[3], Jing Su[4], Ping Yang[4], Enrique R. Batista[4], Christopher J. Dares[1], ***Konstantinos Kavallieratos[1]****, kavallie@fiu.edu. (1) Department of Chemistry & Biochemistry, Florida International University, MIami, Florida, United States (2) Applied Research Center, Florida International University, Miami, Florida, United States (3) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States (4) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

A critical issue in the nuclear fuel cycle is the separation of actinides (An) from lanthanides (Ln) in used nuclear fuel. Minor actinide removal can help reduce long-term toxicity and storage time from thousands of years to just a few hundred years. An(III) and Ln(III) have similar ionic radii and thus their selective separation via solvent extraction presents problems. However, the presence of 5f electrons gives An(III) a somewhat “softer” character relative to Ln(III), and presents a strategy for separation, by using soft binding sites. Herein we present the synthesis and binding properties of amide and thioamide ligand frameworks with soft N-, S- and mixed donor binding sites for selective separation of An from Ln. These ligands are either: i) tripodal pyrazoles containing amide or thioamide groups or ii) dipicolinamide (DPA) and dithiopicolinamide derivatives. Preliminary studies by NMR, UV-VIS, fluorescence spectroscopy, and density functional theory indicate that DPA amide derivatives complex Ln(III) much stronger than their thioamide analogs, and that both thioamide and amide DPA analogs form complexes with UO_2^+ in the gas phase with 2:1 and 1:1 stoichiometries.

NUCL 29

Intensification of liquid–liquid two-phase mass transfer in a high-throughput oscillating feedback micro extractor

***Tingliang Xie**, xtl18745028219@163.com, Cong Xu. Tsinghua University, Beijing, China*

An oscillating feedback micro extractor comprised of an inlet channel, two Coanda steps, a diverging chamber, two feedback channels, a splitter, and an outlet channel was designed using the Coanda effect. The mass transfer performance was investigated in a texting system using a 30% tributyl phosphate-kerosene solution as the organic phase and a 3-mol/L HNO_3 solution as the aqueous phase. The parameters which impact on mass transfer such as the volumetric flux of immiscible liquid–liquid two phases and the structure of the feedback channel were investigated. The experimental results indicated that the arrangement of asymmetric feedback channels had better extraction performance owing to the more unbalanced transverse forces. In addition, the extraction efficiency (acid distribution coefficient/equilibrium acid distribution coefficient) increased with the increase of Reynolds number, and almost complete extraction was achieved using the asymmetric feedback channels. The overall volumetric mean mass transfer coefficients were two or three orders of magnitude higher than those traditional liquid-liquid large-scale extractors.

NUCL 30

Untangling intermediate products in flux-derived *f*-element borates

***Alexander Chemey**, atchemey@gmail.com. Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Boric acid flux reactions with lanthanide and actinide trichlorides have yielded new structures and insights into the production of the *f*-borates. These reactions proceeded at significantly lower temperatures than previous experiments and for a much shorter duration. Indeed, prior reactions with the same starting materials produced only two lanthanide products, but each actinide from plutonium to californium yielded a unique product. There was no systematic answer for why one structure was preferred over another, so by manipulating the reaction conditions, intermediate phases have been sequentially isolated and characterized.

One new product is a neodymium hexaborate chloride which is analogous to a series of lanthanide hexaborate bromides. An americium hexaborate chloride which is isomorphous to this new neodymium product has been obtained as the first kinetic product in the americium chloride-boric acid system. The second americium borate phase is isomorphous with a known samarium borate, and is notable for excluding all chlorides which were present in the starting material. Further studies are pending as of submission of this abstract, and we anticipate presentation of further new actinide structures as well. This presentation will discuss the new structures and argue for the reaction order presented.

NUCL 31

Effects of pi donation on the inverse trans influence

Scott A. Pattenaude*, spattena@purdue.edu, Matthias Zeller, Suzanne C. Bart. Department of Chemistry, Purdue University, West Lafayette, Indiana, United States*

Due to the complex mixture in spent nuclear fuel, transformation of the constituents is particularly challenging. Robust actinyl species, e.g. UO_2^{2+}, are particularly difficult to chemically transform and isolate due to their strongly-bound, trans-oxo ligands. The inverse trans influence (ITI), a consequence of 5f orbital mixing that results in thermodynamic stabilization of a ligand trans to another strongly bound ligand, governs the bond strength, arrangement, and subsequent chemistry of these oxo species.

The ITI not only dominates actinyl bonding, but also extends to imido analogues. Our group has thoroughly explored the synthesis of these imido analogues to gain a better understanding of bonding preferences around heavily pi loaded uranium centers. Recently, we synthesized uranium tris(imido) complexes that lack bulky ancillary ligands, and structural characterization of $U(NDIPP)_3(THF)_3$ shows a facial octahedral uranium ion where no imido groups are oriented trans to each other, supporting the hypothesis that the ITI could be overcome by heavy pi donation. Additionally, with the synthesis and full characterization of a family of uranium tetra(imido) dianions, we demonstrated that an additional imido substituent further deactivates the ITI. These uranium tetra(imido) species serve as models that

demonstrate increasing the number of pi bonded substituents is a general strategy to weaken the strong ligand bonds known to occur from the ITI, and thus enhancing subsequent reactivity of these ligands.

In our current work, we have been seeking to apply this approach to the direct activation of uranyl species. In this strategy, the ITI may be overcome by weakening the strong U-O bonds in the uranyl from the addition of pi donor substituents to the equatorial plane. Furthermore, we have sought to generate transuranic imido analogs in order to uncover periodic trends that relate to the origins of the ITI. This comparison should also give insights to general periodic trends across the actinide series that could be exploited for waste separation.

NUCL 32

Assessment of radiation dose to workers from depleted uranium containing radioactive waste

***Jongseong Lee**, jongseong@kins.re.kr. Korea Institute of Nuclear Safety, Daejeon, Korea (the Republic of)*

Depleted uranium contains a lower fraction of ^{235}U than natural uranium. It has a lower radiation risk due to its lower fraction of ^{235}U. In the 1980s, it was used as a catalyst for producing acrylonitrile in Korea. It has no longer been used after the 2000s. However, approximately 7,000 drums of radioactive waste containing depleted uranium has been stored factory site since that time.

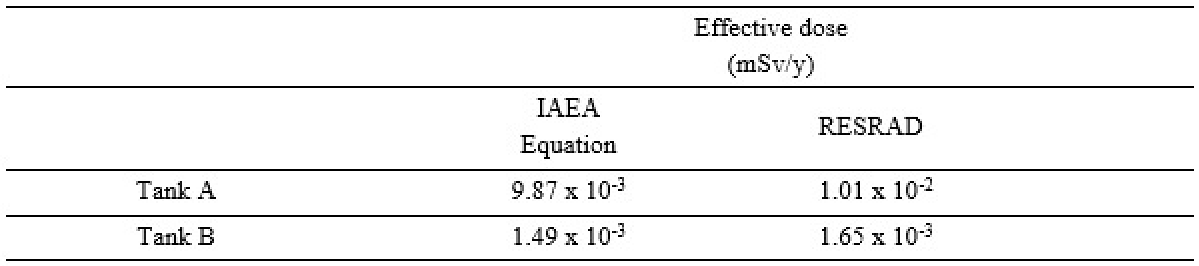
In this report, a radiation risk assessment of radioactive waste containing depleted uranium was conducted to search for disposal schemes in the near future. RESRAD was used to calculate the dose of workers from the radioactive waste tank. Furthermore, the effective dose equation from an IAEA report was used to calculate the dose from the waste. The storage tank geometric features and activity was measured using samples from a tank. Work hours were assumed to be 2,000 hours per year. Distance from the tank during the work was assumed to be 1 m. Default values provided by the RESRAD program were applied to other factors.

Dose calculation was conducted by both a RESRAD and the dose equation. Table 1 shows the effective dose results of both methods. The effective dose limit value in the Korean Nuclear Safety Law is 100 mSv per 5 years for workers and 1mSv for the public. Compared to the dose results, both are quite low values. The radiation risk from the tank thus could be deemed safe for workers.

Although the radiation risk was assessed to be low, depleted uranium has chemical toxicity because it is a heavy metal element and it could thereby

cause problems when storing large amounts of radioactive waste over a long-term period at a factory site. In addition, it contains radionuclides, and hence can lead to concerns among citizens around the storage site. Furthermore, for the systematic management of radioactive waste, the depleted uranium should be delivered to low-level waste disposal site.
However, this radioactive waste is not included as a disposal subject in the current low-level waste disposal site delivery and disposal scheme. Depleted uranium is mixed with waste in sludge form, and it should be transformed to a solid form to be delivered. To manage the radioactive waste, specifically including waste transformation and volume reduction, the disposal subject scheme should be revised in the near future.

Table 1 Effective dose results



	Effective dose (mSv/y)	
	IAEA Equation	RESRAD
Tank A	9.87×10^{-3}	1.01×10^{-2}
Tank B	1.49×10^{-3}	1.65×10^{-3}

NUCL 33

Influence of inner- and outer- coordination sphere interactions on the structural chemistry of actinide(IV) chloride complexes

***Karah E. Knope**, kek44@georgetown.edu. Chemistry, Georgetown University, Washington, District of Columbia, United States*

Actinide-ligand interactions underpin a number of technologically and environmentally relevant processes including separations chemistries, the transport of heavy elements, and waste disposal strategies. In all of these cases, an understanding of the conditions over which different solution species are stable or precipitated is critically important to the development of reliable models that accurately predict the chemical properties of these radionuclides. Characterization of the precipitated phases may afford insight into metal-ligand interactions that govern the complexation, redox, precipitation, and overall chemical behavior of the metal ion. Within this context, we are examining the solution and solid-state structural chemistry of tetravalent actinide (Th and U) materials obtained from high chloride media. Presented here will be an overview of recent efforts to probe the effects of

both inner- and outer- coordination sphere interactions on the structural chemistry of tetravalent actinides. How the synthetic conditions, identity of the counter-ions, and nature of complexing ligands affect the speciation of the solid-state Th(IV)- and U(IV)-building units will be discussed.

NUCL 34

Composite metal-organic frameworks modified membranes for liquid-phase filtration adsorption of uranium

***Boxuan Yu**[1], moying1418@163.com, Gang Ye[1,2], Jing Chen[1,2]. (1) Collaborative Innovation Center of Advanced Nuclear Energy Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China (2) Beijing Key Lab of Radioactive Waste Treatment, Tsinghua University, Beijing, China*

Developing facile and robust technologies for effective enrichment of uranium from aqueous systems is of great significance for resource sustainability and environmental safety. Recently, metal–organic frameworks (MOFs) have emerged as a type of porous material with significant prospects for addressing current challenges pertinent to energy and environmental sustainability. In this work, with the assistance of polydopamine (PDA), a series of MOFs were in-suit deposited in the channels of track-etched membranes (TMs) by method named contra-diffusion synthesis, and some composite membrane were undergoing a secondary growth period for increasing loadage of MOFs. One-dimensional MOFs nanowires or nanotubes were obtained and among them HKUST-1 ($Cu_3(BTC)_2$) composite membranes exhibit high filtration adsorption capacity to uranium (269.2mg/g). In this type of composite membrane, the PDA layer act as the nucleation center of MOFs deposition, inducing the HKUST-1 nanocrystal to adhere to the wall of channels rather than nucleating in the channels and grow up to black the channel. The results show that composite membrane (TMs-HKUST-1-B) expressed strong adsorption ability on U(VI) compared with raw TMs and semi-prepared samples (TMs-HKUST-1-A) that did not undergo seacondary growth presented in Fig. 1, which may be accounted for combined interactions of -COOH and suitable channel size. According to the N_2 sorption–desorption experiments, TMs occurred a sharply increase on specific surface area after modification and SEM showed that the MOFs crystals(<100nm) in the channel were much smaller than ordinary one(>5μm), which may raise the utilization rate of active coordination sites.

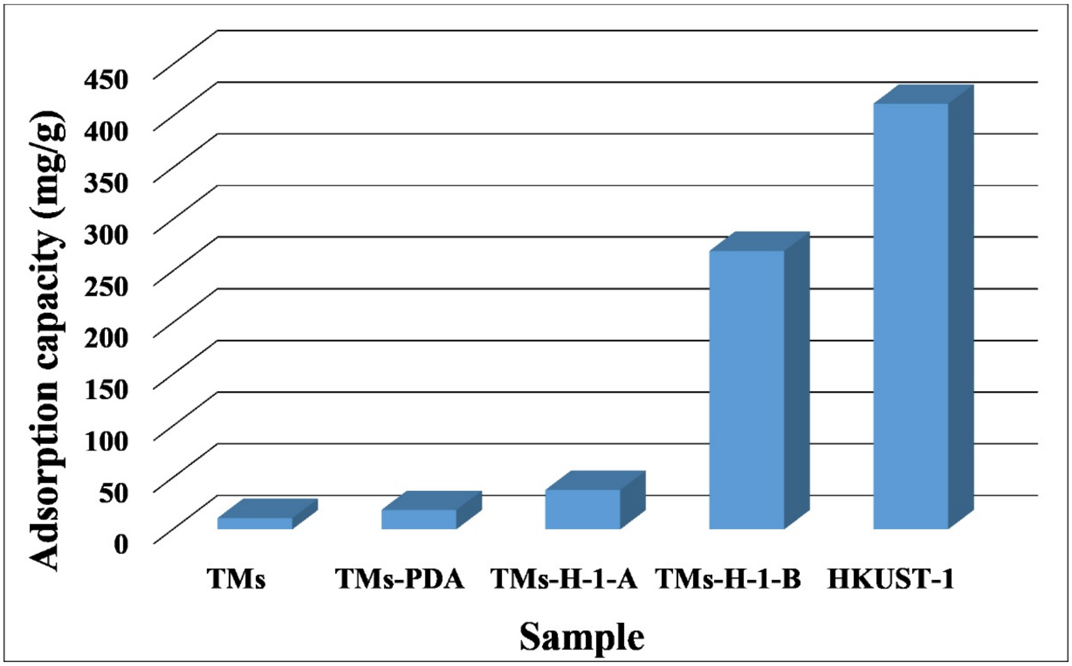


Figure 1. U(VI) adsorption by HKUST-1 modified composite TMs, compared with the performance of HKUST-1 crystal, raw and semi-prepared samples.

NUCL 35

Formation of metallic nanoparticles in a ceramic matrix

Ram Devanathan, *ram.devanathan@pnnl.gov, Michele Conroy, Weilin Jiang. Pacific Northwest National laboratory, Richland, Washington, United States*

Ceramics offer a desirable combination of physical and chemical properties for applications in extreme environments. We have examined the fundamental mechanisms governing the formation of metal nanoparticles in a ceramic matrix relevant to nuclear waste forms. We synthesized ceria films doped with metals, such as Mo, and subjected them to a variety of extreme processing conditions including ion bombardment and annealing at temperatures up to 1350 K. We used atomistic simulation to complement the synthesis and high resolution electron microscopy characterization efforts. The results offer insights into the effect of external stimuli on chemical and microstructural changes in ceramics.

NUCL 36

Spectroscopic characterization of Tc(I) tricarbonyl species relevant to the Hanford tank waste

Tatiana G. Levitskaia[1]*, tatiana.levitskaia@pnl.gov, Sayandev Chatterjee*[2]*, Yingge Du*[4]*, Mark Engelhard*[5]*, Gabriel B. Hall*[3]*, Eric D. Walter*[6]*, Nancy M. Washton*[7]*. (1) Battelle Pacif N West Natl Lab, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States (3) Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona, United States*

Technetium-99 (Tc) generated from the fission of ^{235}U and ^{239}Pu in high yields is one of the most difficult contaminants to be addressed at the U.S. Department of Energy (DOE) Hanford Site. Among radioactive contaminants, Tc presents a unique challenge in that it has a long half-life, exhibits diverse chemical properties and typically highly mobile in the environment leading to several uncertainties regarding treatment and disposition options. The complex behavior of Tc under storage, treatment, and immobilization conditions significantly affects its management options. The overall objective of the Technetium Management program at Pacific Northwest National Laboratory is to provide the DOE Office of Environmental Management with practical solutions to Tc needs encountered in the processing of Hanford tank waste and vadose zone remediation; and technical activities are being performed in the areas of Tc characterization, treatment, and disposition. One specific task is focused on elucidation of the identity and properties of non-pertechnetate species in the liquid Hanford tank waste. Previous analysis of the tank waste samples provided strong evidence that non-pertechnetate species can be comprised of $Tc(CO)_3^+$ complexes containing Tc in oxidation state +1. This paper describes our current results on the development of spectroscopic library of Tc(I) tricarbonyl species for their characterization and identification in the Hanford tank wastes.

NUCL 37

Oxidative stabilities of low-valent technetium species relevant to their separations from Hanford tank waste

Sayandev Chatterjee*, rasayan@gmail.com, Tatiana Levitskaia, Gabriel B. Hall, Yingge Du, Mark Engelhard, Nancy M. Washton, Vaithialingam Shutthanandan, Eric D. Walter. Pacific Northwest National Laboratory, Richland, Washington, United States*

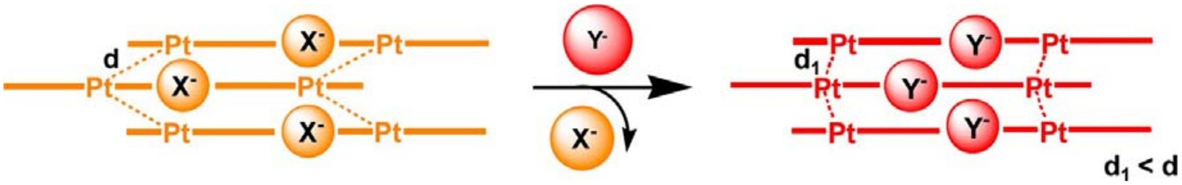
The radioelement technetium-99 (^{99}Tc) is a major contaminant found in nuclear tank waste stored at the U.S. Department of Energy (DOE) site at Hanford, Washington. Existing predominately in the liquid supernatant and salt cake fractions, it is among the most difficult contaminants to dispose of and/or remediate because of its complex chemical and redox behavior in tank waste, limited incorporation in the glass waste forms during mid- to high-temperature immobilization processes, and high mobility in the environment. Although in solution ^{99}Tc can have oxidation states ranging from +7 to 1, it is observed to prefer existing as pertechnetate (TcO_4^-) (oxidation state VII) in strongly alkaline environments under ambient atmospheric conditions. Therefore, TcO_4^- is expected to be the significantly dominant fraction in the highly alkaline multi-component matrices of Hanford tank waste supernatant fractions. However, contrary to general expectations based on existing knowledge in Tc chemistry, a dominant fraction of the soluble Tc in the waste supernatants with high organics content occurs as low-valent Tc (oxidation state < +7), most notably EXAFS observations suggested potential presence of Tc(I) carbonyl species in addition to Tc(IV) and Tc(VI). Understanding the mechanisms of generation of these non-pertechnetate species *in-situ* as well as evaluating their *ex-situ* stabilities under ambient atmospheric conditions are key to design new methods for their effective separation and remediation. One approach of separation of non-pertechnetate species is their oxidation to TcO_4^- and subsequent separation by ion-exchange methods. Towards this goal, this work evaluates the oxidative stabilities of non-pertechnetate complexes generated *ex-situ* under conditions relevant to Hanford tank wastes, such as multicomponent brine-like alkaline solution matrices. Toward elucidation of the mechanism of formation of low-valent Tc species, pathways of *in-situ* reduction of pertechnetate in these solutions are investigated using CO/H_2 as a reactant at elevated pressure and temperature.

NUCL 38

Highly selective detection of aqueous pertechnetate using square-planar platinum(II) complexes

Sayandev Chatterjee[2]*, rasayan@gmail.com, Amie E. Norton*[4]*, William B. Connick*[3]*, Thomas E. Albrecht-Schmitt*[1]*, Tatiana Levitskaia*[2]*. (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States (3) Univ of Cincinnati, Cincinnati, Ohio, United States (4) Chemistry, University of Cincinnati, Cincinnati, Ohio, United States*

The selective detection of anions in complex multicomponent matrices remains challenging. Of particular interest is recognition of toxic and/or radioactive pertechnetate (TcO_4^-), a dominant environmental chemical form of the radioisotope ^{99}Tc produced in the nuclear fuel cycle. The long half-life of ^{99}Tc (2.13×10^5 years) and highly mobile subsurface transport properties of $^{99}TcO_4^-$ generate considerable environmental and health concerns. Monitoring ^{99}Tc in groundwater is challenging due to the requirement to meet low detection limits below the drinking water standard as well as presence of competing anions. This work focuses on square-planar, cationic, coordinatively unsaturated Pt(II) complexes that undergo a distinct spectroscopic change upon exposure to $^{99}TcO_4^-$. The spectroscopic response arises from the ability of these complexes to form quasi-one-dimensional stacked systems via noncovalent Pt---Pt interactions, which can be altered by varying the counter anion. In the parent solid material, Pt(II) units are arranged in a manner that does not result in a continuous chain of short Pt---Pt contacts. Substitution of an anion, that uniquely satisfy the requirements of lattice parameters needed for extended Pt---Pt overlap (as shown in attached scheme), result in distinct spectroscopic changes in the material. These form the basis of anion detection, and can be customized for TcO_4^- detection. Our studies identified the Pt(II) complex $[Pt(tpy)Br]SbF_6$ (tpy = 2,2′;6′,2″-terpyridine) to undergo a dramatic colorimetric / luminescence response upon TcO_4^- exposure due to concomitant enhancement of Pt---Pt interactions. The spectroscopic response was highly selective for TcO_4^- among other competing anions (Cl^-, CO_3^{2-}, SO_4^{2-}, NO_3^-) indicating TcO_4^- to uniquely satisfy the steric and electronic requirements for an extended chain of stacked square-planar $[Pt(tpy)Br]^+$ units. The electronic spectroscopies were complimented by structural determination to elucidate the mechanism of this response at a molecular level.



Scheme 1. Change in Pt---Pt interactions due to a simple X^-/Y^- anion exchange

NUCL 39

f-Block borates: From structure evolution to new separation methods

***Thomas E. Albrecht-Schmitt**, talbrechtschmitt@gmail.com. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

In this talk the synthesis, structures, spectroscopy, and stability of f-block borates will be discussed. In particular, the lanthanide and actinide series will be contrasted from one another. We will demonstrate that the amplification of minor differences in bonding at the metal centers can be utilized for the separation of lanthanides from one another via a simple, green method.

NUCL 40

Influence of organic ligands on Pu sorption to mineral surfaces: Characterization of aging processes and ternary complexes

***Brian A. Powell**[1], bpowell@clemson.edu, Nathan Conroy[1], Jennifer Wong[1], Annie Kersting[2], Mavrik Zavarin[2]. (1) Environmental Engineering and Earth Sciences, Clemson University, Clemson, South Carolina, United States (2) Seaborg Institute, Lawrence Livermore Natl. Lab., Livermore, California, United States*

Sorption of plutonium (and other actinides) to mineral surfaces represents the primary means by which migration of plutonium is slowed in the subsurface. Over the past several decades, our understanding of sorption mechanisms and the species involved have greatly increased. Of particular interest to this work is the influence of organic ligands on the sorption of plutonium to iron oxide minerals. Due to co-adsorption of the organic ligands, ternary surface-ligand-Pu complexes may form in low pH systems which will increase sorption of Pu relative to ligand free systems. Conversely, increasing pH appears to stabilize aqueous Pu-ligand complexes which causes a decrease in sorption relative to a ligand free system and could result in enhanced subsurface migration of Pu. These interactions are identified through kinetic sorption/desorption experiments along with an additional aging process which appears to enhance the stability of surface bound Pu over time. The implications of these findings with respect to far field transport of Pu will be discussed.

NUCL 41

^{15}N Pulsed EPR experiments on lanthanides and actinides bis-triaziynl pyridine (BTP) complexes

***David Dan**, dd15g@my.fsu.edu, Thomas E. Albrecht-Schmitt. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Over the next decade understanding how to separate short and long-lived isotopes from nuclear waste streams will be an ever-increasing problem. Bis-triazinyl Pyridines (BTP) are a good candidate for such separations. These studies will focus on the *f* elements Amerecium (Am), Europium (Eu), and Neodymium (Nd). Earlier work with BTPs have shown separation factors of greater than 100 for Am(III) over Eu(III). Looking at why and how this family of ligands binds to lanthanides and actinides will help in future ligand design. Pulsed EPR experiments such as ^{15}N electron spin echo modulation (ESEEM) and 2D hyperfine sub-level correlation (2D HYSCORE) will be carried out to show the extent of covalency and how strongly these ligands bind to actinides and lanthanides. Also, single crystal x-ray diffraction will reveal how these ligands are complexing with these heavy elements.

NUCL 42

Defect perovskites for the sequestration of volatile nuclear waste

***Spencer M. Scott**, sscottNE@gmail.com, Weiguang Zhu, Jie Lian. Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States*

The perovskite mineral structure, ABX_3, has drawn attention for the incorporation of actinides into a durable nuclear waste form, primarily as a component of SYNROC, a leading technology in the disposal of actinides. Defect perovskites, which follow the chemical formula A_2BX_6, have primarily drawn the attention of the photovoltaic community as a hole-transport material. However, defect perovskites are capable of high (up to 66 wt %) halogen mass loadings, notably Cl and I, which represent serious challenges in the disposal and reprocessing of spent nuclear fuel. Cs_2SnCl_6, a defect perovskite molecular salt which displays air stability and water insolubility, is highly attractive for nuclear waste disposal due to a combination of a high mass loading of both Cs (44.6 wt %) and Cl (35.6 wt %), as well as thermal stability above 600 ^{o}C. Through spark plasma sintering (SPS), a field assisted sintering technique (FAST), Cs_2SnCl_6 powders were consolidated into a fully dense ($\geq$ 94% t.d.) pellet without any decomposition occurring. This enabled the preservation of the water insoluble phase, and the retention of the volatile chlorine and cesium after consolidation. Other defect perovskite compositions are being researched for nuclear waste applications, including Cs_2SnI_6 for the disposal of ^{129}I, and K_2SnCl_6 for the disposal of pyroprocessing waste.

NUCL 43

Actinide target/source preparation and use in the Physics Division at ANL

John P. Greene, *greene@anl.gov. Physics, Argonne National Laboratory, Argonne, Illinois, United States*

Radioactive targets, and in some cases, sources of the actinide nuclides are frequently requested for low-energy nuclear physics research and for experiments carried out using heavy-ion accelerators. At the Argonne National Laboratory (ANL) Physics Division, preparation and handling of these actinide targets/sources is accomplished using a variety of techniques. For heavy element research at the ATLAS facility, stable targets are produced by physical vapor deposition (PVD) while the actinide species are deposited via the technique of molecular plating. Important aspects of this work include the availability of the isotopes of the actinide elements and the ability to assay them accurately. Here we present some recent research highlights which involved the use of a variety of actinide elements with specific examples of targets/sources beyond curium.

NUCL 44

Improving extraction of +4 actinides

Samantha K. Schrell *[4], sschrell@lanl.gov, Maksim Livshits[5], Justin N. Cross[3], Maryline Ferrier[2], Veronika Mocko[3], Benjamin W. Stein[1], Kevin T. Bennett[1], Brian L. Scott[3], Jeffrey Rack[5], Stosh A. Kozimor[3]. (1) C-IIAC, Los Alamos National Laboratories, Santa Fe, New Mexico, United States (2) Chemistry - Inorganic Isotope and Actinide Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (4) C-IIAC, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (5) Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico, United States*

One substantial challenges in actinide separation science is associated with programmatic needs to isolate microscopic amounts (10^{10} atoms) of high purity (99.9999%) Np from macroscopic quantities (gram to kilogram) of U and

Pu. There are additionally scenarios where microscopic amounts of Pu needs to be isolated from bulk uranium matrixes. These separations are complicated by quantity differences between the analyte (Np or Pu) versus the contaminate (U + Pu or U, respectively). Currently, programmatic methods rely on bulk extraction of Np using the thenoyltrifluoroacetone (TTAH) chelate (Figure 1). Unfortunately, the extraction is unreliable and generates large quantities of organic radioactive waste. When this extraction works, it is quite effective at selectively removing the desired actinide analyte from the bulk matrix. Hence the TTA extraction has become known in the community as the "best of the worst" solution to the An^{IV}/An^{IV} purification problems.

This presentation will represents the first in a series of studies focused on advancing understanding of the TTAH extraction processes for +4 metal ions. Herein, we have rigorously characterized a series of $M^{IV}(TTA)_4$ (M = Zr^{IV}, Hf^{IV}, Ce^{IV}, Th^{IV}, U^{IV}, Np^{IV}, and Pu^{IV}) and $M^{III}(TTA)_4{}^{1-}$ (M = Ce^{III}, Nd^{III}, Sm^{III}, and Yb^{III}) coordination complexes. Although, *Prasad* and co-workers first prepared many of these compounds in 1966, numerous chemical properties were not characterized, such as their solid-state structure and solution-phase behavior. Our contribution will detail convenient methods to prepare the $M(TTA)_4{}^{x-}$ (x = 0, 1) compounds. Additionally, we will discuss the using these $M(TTA)_4{}^{x-}$ (x = 0, 1) compounds as standards to facilitate characterization the organic phase of an actual TTAH extraction of Pu^{IV} and Np^{IV} into *o*-xylene from hydrochloric acid.

NUCL 45

Exploring oxidation states of berkelium and californium in the gas phase

***John K. Gibson**[2], jkgibson@lbl.gov, Monica Vasiliu[4], Phuong D. Dau[3], Kirk A. Peterson[6], Attila Kovács[1], David A. Dixon[5]. (1) Institut for Transuranium Elements, Eggenstein-Leopoldshafen, Germany (2) Lawrence Berkeley National Laboratory, Emeryville, California, United States (3) Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California, United States (4) Chemistry, The University of Alabama, Tuscaloosa, Alabama, United States (5) Chemistry Dept, Shelby Hall, The University of Alabama, Tuscaloosa, Alabama, United States (6) Washington State University, Pullman, Washington, United States*

Regarding their dominant chemical properties, the transcurium actinides Bk and Cf largely resemble the homologous trivalent lanthanides, Tb and Dy. However, important divergences appear, including the Bk(IV), Cf(II) and Cf(IV) oxidation states. Even higher oxidation states, particularly Bk(V) and Cf(V), are plausible in view of the relatively high energies of the 5f electrons that must be chemically accessible to achieve these states. Gas-phase chemistry enables assessment of intrinsic stabilities of known oxidation states of Bk and Cf, from +II to +IV, as well as of as yet unknown oxidation states such as Bk(V) and Cf(V). The interaction between challenging experiments and high-level relativistic theory for elementary gas-phase binary oxides and small complexes provides fundamental insights into distinctive aspects of 5f-element chemistry for actinides beyond curium.

NUCL 46

Atomic physics studies of heaviest elements

Michael Block[1,2]*, m.block@gsi.de. (1) Superheavy Element Physics, GSI Helmholtzzentrum, Darmstadt, Germany (2) Superheavy Element Physics, Johannes Gutenberg University, Mainz, Germany*

The heaviest elements with $Z > 100$ attract interest from nuclear and atomic physics due to their distinct properties. Nuclear shell effects are responsible for their very existence stabilizing them against immediate disintegration by spontaneous fission. Strong relativistic effects influence their electronic structure and chemical behavior as certain orbitals are stabilized while others become less bound. Precision measurements of different atomic and nuclear properties improve our understanding of these exotic objects and probe the nature of the underlying forces. Accurate experimental data also challenge theoretical predictions and contribute to their improvement. Numerous precision measurements of ground-state properties of radionuclides across the nuclear chart have been obtained in recent years utilizing ion-trap and laser spectroscopy-based techniques. New methods for slowing down high-energy beams in buffer gas cells have opened the door to extend such techniques to the heaviest nuclides. I will discuss such developments and present recent results on atomic and nuclear properties of nobelium isotopes obtained at the GSI in Darmstadt, Germany.

NUCL 47

X-ray absorption spectroscopy of actinium and comparison with actinide +3

Maryline Ferrier[1]*, mferrier@hotmail.com, Benjamin W. Stein*[1]*, Enrique R. Batista*[2]*, John M. Berg*[3]*, Eva R. Birnbaum*[3]*, Justin N. Cross*[1]*, Jonathan W. Engle*[4,1]*, Stosh A. Kozimor*[1]*, Juan S. Lezama Pacheco*[5]*. (1) Chemistry*

Division, Los Alamos National Lab, Los Alamos, New Mexico, United States (2) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (4) University of Wisconsin, Madison, Wisconsin, United States (5) Stanford University, Stanford, California, United States

Actinium-225 is a promising isotope for targeted alpha therapy. Unfortunately, progress in developing chelators for medicinal applications has been hindered by a limited understanding of actinium chemistry. This knowledge gap is primarily associated with handling actinium, as it is highly radioactive and in short supply. Hence, Ac^{III} reactivity is often inferred from the lanthanides and minor actinides (i.e. Am, Cm), with limited success. Recent upgrades and technological improvements at synchrotron facilities have provided new opportunities to overcome challenges associated with characterizing the coordination chemistry of actinium. Herein, we will present application of these new spectroscopic capabilities to conduct the first actinium X-ray absorption fine structure (XAFS) studies. Results will be compared with analogous measurements made on actinides in the +3 oxidation state. Spectra interpretations, guided by molecular dynamics-density functional theory (MD-DFT) calculations, will also be discussed. These results imply diverse reactivity for the +3 actinides and highlight the unexpected and unique Ac^{III} chemical behavior.

NUCL 48

Chemical studies of Fl (element 114): Heaviest chemically studied element

Lotte Lens[1,3], *L.Lens@gsi.de, Alexander Yakushev*[3,4], *Christoph Duellmann*[1,3], *Masato Asai*[5], *Michael Block*[3,1], *Helena May David*[3], *John D. Despotopulos*[6], *Antonio Di Nitto*[1,3], *Klaus Eberhardt*[1,4], *Michael Goetz*[4,3], *Stefan Goetz*[4,3], *Hiromitsu Haba*[7], *Laura Harkness-Brennan*[8], *Fritz-Peter Hessberger*[3,4], *Rolf-Dietmar Herzberg*[8], *David Hinde*[9], *Jan Hoffmann*[3], *Huebner Annett*[3], *Egon Jaeger*[3], *Daniel Judson*[8], *Khuyagbaatar Jadambaa*[3,4], *Birgit Kindler*[3], *Joonas Konki*[10], *Jens Volker Kratz*[1], *Jörg Krier*[3], *Nikolaus Kurz*[3], *Mustapha Laatiaoui*[11], *Susanta Lahiri*[12], *Bettina Lommel*[3], *Momita Maiti*[13], *Andrew K. Mistry*[4,3], *Christoph Mokry*[1,4], *Ken Moody*[6], *Yuichiro Nagame*[5], *Jon P. Omtvedt*[2], *Philippos Papadakis*[10], *Valeria Pershina*[3], *Dirk Rudolph*[14], *Jörg Runke*[1,3], *Matthias Schaedel*[3], *Paul Scharrer*[4,3], *Tetsuya Sato*[5], *Dawn A. Shaughnessy*[6], *Brigitta Schausten*[3], *Jutta Steiner*[3], *Petra Thörle-Pospiech*[1,4], *Norbert Trautmann*[1], *Kazuaki Tsukada*[5], *Juha Uusitalo*[10], *Andrew Ward*[8], *Maciej Wegrzecki*[15], *Elizabeth Williams*[9], *Norbert Wiehl*[1], *Vera*

Yakusheva[3,4]. (1) Johannes Gutenberg University Mainz, Mainz, Germany (2) Dept. Chemistry, University of Oslo, Oslo, Norway (3) GSI Helmholtzzentrum für Schwerionenforschung , Darmstadt, Germany (4) Helmholtz-Institut Mainz, Mainz, Germany (5) JAEA, Tokai, Japan (6) LLNL, Livermore, California, United States (7) RIKEN, Wako-shi, Japan (8) University Liverpool, Liverpool, United Kingdom (9) ANU, Canberra , Australian Capital Territory, Australia (10) University Jyväskylä, Jyväskylä, Finland (11) KU Leuven, Leuven, Belgium (12) SINP, Kolkata, India (13) IITR, Uttarakhand, India (14) University Lund, Lund, Sweden (15) ITE, Warsaw, Poland

The atomic properties of transactinide elements are pronouncedly influenced by strong relativistic effects. The heaviest element under current chemical study is flerovium (Fl, element 114). Early atomic calculations indicated this to be chemically inert, similar to noble gases. More recent relativistic calculations suggest a distinct metallic character, but lower reactivity than its lighter homolog, Pb. Experimental studies are challenging due to low production rates and short half-lives. In addition, a wide volatility range, from the rather reactive and non-volatile metal Pb, to the inert and noble gas Rn, has to be covered, and detection of single atoms has to be achieved. For the latter, the use of a physical pre-separator is advantageous, as it provides a significant background reduction.

Based on the observation of three radioactive decays attributed to Fl in a first Fl chemical study performed by a PSI-FLNR collaboration, a weak interaction with gold was inferred. In a second study, performed by a collaboration working at the TASCA preseparator at GSI, Darmstadt, two Fl atoms were observed. The results pointed to the formation of a metal-metal bond of Fl with gold, but the limited statistics allowed to derive only a lower limit for the interaction strength. The contradicting results called for advanced studies. Additional experiments performed by the PSI-FLNR collaboration, did not result in Fl observation.

Two new experimental campaigns were performed at TASCA in 2014 and 2015, where further Fl atoms were observed. In this talk, the current status of chemical studies of Fl will be discussed.

NUCL 49

Einsteinium-255 generator for off-line studies of fermium-255?

***Christoph Duellmann**[2,3], duellman@uni-mainz.de, Michael Block[1,2], Klaus Eberhardt[4,5], Sebastian Raeder[5,6], Dennis Renisch[2,5], Norbert Trautmann[2], Klaus Wendt[2]. (2) Institute of Physics, Johannes Gutenberg University Mainz, Mainz, Germany (3) GSI Helmholtzzentrum fuer Schwerionenforschung,* *Darmstadt, Germany (4) Institute of Nuclear Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany (5) Helmholtz Institute Mainz, Mainz, Germany*

The heaviest elements available in macroscopic amounts, e.g., from ORNL, are einsteinium (element 99) and fermium (element 100). Typical isotopes include Es-254 (half-life: 276 d), available in microgram quantity, and Fermium-257 (half-life: 100 d), available in picogram quantity. Further einsteinium isotopes are produced concurrently, including Es-253 (20.5 d) and Es-255 (40 d). These, however, decay largely during a six-month cooling period following irradiation, prior to the chemical separation. Nuclear decay properties in this region of the chart of nuclides provide for the possibility of producing a generator system based on 40-d Es-255, which has a 92% beta-minus decay branch, leading to 20-h Fm-255. In contrast to the situation in which Fm-255 is chemically isolated and vanishes with its short half-life, the availability of Es-255 precursor would allow for a constant milking of the Fm-255 daughter over a timeframe of many weeks, thus enabling more sophisticated studies of this element, even without the need of a dedicated Fm separation from the irradiated fuel. In a first optical experiment on Fm, for example, a sample of 2.7E10 atoms served for the first identification of atomic levels in Fm. The short 20-h half-life, though, precluded more extensive studies. With this contribution we like to highlight the opportunities that would arise from the availability of a sample enriched in Es-255. The resulting long-term availability of Fm-255 would allow, e.g., for highlight studies of its atomic structure, in the spirit of the pioneering studies performed in Mainz in 2002, or for ultra-precise state-of-the-art atomic mass measurements employing Phase-Imaging Ion-Cyclotron-Resonance Mass Spectrometry.

NUCL 50

Theoretical exploration of covalency in heavy actinides

***Morgan Kelley**, m.kelley@wsu.edu, Enrique R. Batista, Ping Yang. Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Actinide chemistry has long puzzled scientists due to the complicated role of 6d- and 5f- electronic configurations in actinide-ligand bonding, chemical reactivity, and both their spectral and magnetic properties. In recent years, the covalent interactions of heavy actinides with chelating ligands have been the subject of much debate, with the difficulty of conducting experiments in this part of the periodic table preventing exhaustive investigation. We have used density functional theory to investigate covalency in actinide-ligand bonds across the actinide series in two different model systems: the biological decorporation ligand 3,4,3-LI(1,2-HOPO) and dipicolinate. Changes in covalent interactions across the actinide series are investigated, offering new insights into the complexation of the late actinides and guiding principles for the design of new chelating ligands.

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Ionization potential measurements of the heaviest actinides

Tetsuya K. Sato, *sato.tetsuya@jaea.go.jp. Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki, Japan*

The first ionization potential (IP_1) yields information on valence electronic structure of an atom. IP_1 values of heavy actinides beyond einsteinium (Es, $Z = 99$), however, have not been determined experimentally so far due to the difficulty in obtaining these elements produced in nuclear reactions on scales of one atom at a time.
Recently, we successfully determined the IP_1 value of the heaviest actinide element, lawrencium (Lr, $Z = 103$) for the first time using a surface ionization method. The experimental result has shown that the IP_1 of Lr is distinctly low among actinide elements owing to the configuration of closed $5f^{14}$ and $7s^2$ shells with an additional weakly-bound electron in the valence orbital.
We have applied this method to IP_1 measurements of other heavy actinide elements, nobelium (No, $Z = 102$), mendelevium (Md, $Z = 101$) and fermium (Fm, $Z = 100$). The experiments were conducted with the ISOL (Isotope Separator On-Line) system at the JAEA tandem accelerator facility. The surface ion-source coupled to a He/CdI_2 gas-jet transport system was installed in the ISOL for a surface ionization of isotopes of the heavy actinide elements. We successfully ionized and mass-separated ^{257}No ($T_{1/2} = 24.5$ s), ^{251}Md ($T_{1/2} = 4.27$ min), and ^{249}Fm ($T_{1/2} = 2.6$ min) with ionization efficiencies (I_{eff}) of approximately $(0.5 \pm 0.1)\%$, $(1.2 \pm 0.3)\%$, and $(1.1 \pm 0.2)\%$ at 2800 K, respectively. From the obtained I_{eff}values, the IP_1 values were determined based on the IP_1 dependence of I_{eff} in the surface ionization process. The experimental results are in good agreement with the predicted ones by theoretical and/or semi-empirical calculations. The IP_1 value increased with an atomic number up to No and fell dramatically at Lr, indicating the similar trend with that of heavy lanthanide elements. This behavior clearly indicates that the 5f orbital is filled up at No. Details of the experiments and results will be given in the presentation.

NUCL 52

Exploring redox coordination chemistry in transuranic elements with various crown ethers and cryptands through lanthanides

Frankie D. White[2], *white.deuce@gmail.com, Matthew L. Marsh*[1]*, David E. Hobart*[3]*, Thomas E. Albrecht-Schmitt*[2]*. (1) Florida State University, Louisville, Tennessee, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (3) National Security Education Center, Los Alamos National Laboratory, Santa Rosa Beach, Florida, United States*

Investigating the structure and bonding of the heavier actinides (Am-Es) allows for a better understanding in the type of chemistry these elements undergo compared to the lighter actinides (Ac-Pu). By simply observing the oxidation states of the lighter actinides against the heavier actinides, it can be concluded that the lighter actinides behave differently from their lanthanide counterparts. However, pinpointing exactly where in the in the 5*f* series this difference ends would allow for a better understanding of these heavy elements. Even considering the differences in lanthanides and actinides, lanthanides do serve as great models for coordination and redox chemistry in the actinides because of similar coordination numbers and their $Ln^{3+} \rightarrow Ln^{2+}$ reduction potentials. It has been demonstrated that good chelating ligands and select solvents can create favorable conditions for stabilzing the Ln/An^{+2} oxidation state. By utlizing the redox coordination chemistry behavior in lanthanides, transuranic chemistry can be closely modeled. In particular, samarium serves as an excellent surrogate for modeling californium redox chemistry because of many similarities between the two elements.Through synthesis and electrochemistry, the stabilization of lower oxidation states in transuranic elements through coordination chemistry in non-aqueous solutions and the solid state is explored with various crown ethers and cryptands.

NUCL 53

Electrochemical studies to stabilize divalent californium

Matthew L. Marsh, *mattmarsh0@aol.com, Frankie D. White, David E. Hobart, Thomas E. Albrecht-Schmitt. Florida State University, Louisville, Tennessee, United States*

The element californium represents an important break in the actinide series. Many recent studies have concluded that there are distinct emergent chemical

properties that might relate to its more accessible divalent redox potential. However, scarcity and difficulty with experimental manipulations has precluded an extensive look at the electrochemical properties of this element in solution. Utilizing cyclic voltammetry, spectroelectrochemistry, and other means of characterization with complexants and solvents will be carried out in order to model the similarities and differences of this element with a lanthanide of a similar electrochemical property, samarium. This will enable a better fundamental understanding of the f-elements with the goals of nuclear waste separations and storage needing to be addressed in the coming decades.

NUCL 54

Chelation past curium: Exploring trends in f-orbital bonding

Rebecca J. Abergel[1], *rjabergel@lbl.gov, Gauthier Deblonde*[1], *Julian Rees*[1], *Corwin Booth*[1], *Wibe Dejong*[1], *Roland Strong*[2]. *(1) Lawrence Berkeley National Laboratory, Berkeley, California, United States (2) Fred Hutchinson Cancer Research Center, Seattle, Washington, United States*

Separation of actinides 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. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific transcurium actinide coordination features by bio-inspired catecholamide and hydroxypyridinone hard oxygen-donor ligands. Using such ligands allowed the solution differentiation of Cm, Bk, and Cf, through stabilization of Bk(IV) under mild aqueous conditions. Resulting Cm(III) and Bk(IV) complexes exhibit sensitized luminescence features that provide 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 5*f*-element sequence. Combined with theoretical predictions, these data add significant insight to the field of transcurium chemistry, and may lead to innovative characterization methods and separation processes.

NUCL 55

Redox studies of the heaviest actinides

Yuichiro Nagame, *nagame.yuichiro@jaea.go.jp, Atsushi Toyoshima. Japan Atomic Energy Agency, Tokai, Japan*

Redox studies of the heaviest elements are expected to give valuable information on valence electronic states influenced by strong relativistic effects, such as oxidation states and redox potentials. Well established electrochemical approaches like cyclic voltammetry are, however, not available for the one atom-at-a-time chemistry of the heaviest elements. Thus, one needs to investigate redox properties of the heaviest elements based on the partition behavior of single atoms between two phases instead of measurements of electric currents from redox reactions. A new apparatus for the study of electrochemical properties of the heaviest elements was developed. The apparatus is based on a flow electrolytic cell combined with column chromatography. The working electrode is made of glassy-carbon fibers that are packed in a porous Vycor glass tube which works as an electrolytic diaphragm. The surface of the carbon fibers was chemically modified with Nafion® perfluorinated cation-exchange resin. A platinum (Pt)-mesh counter electrode was placed in the electrolyte pool to surround the glass tube. The potential on the working electrode was controlled using a potentiostat referring to the 1.0 M LiCl-Ag/AgCl electrode placed in the pool. The apparatus was applied to the oxidation of nobelium (No) and the reduction of mendelevium (Md) by controlling the applied potential. We discuss the experimental set-up and the results on the redox reactions of heavy actinides.

NUCL 56

Heavy element chemistry research at Texas A&M University

Charles M. Folden, *Folden@comp.tamu.edu. Cyclotron Institute, Texas A&M University, College Station, Texas, United States*

In recent years, significant effort has been made at Texas A&M University to develop techniques that could be applied to chemical studies of the heaviest elements. This work has largely focused on future chemical studies of nihonium (element 113), which is predicted to be a member of group 13. Initial experiments have focused on the study of the liquid-liquid extraction of the group 13 elements using carrier-free radioactive tracers of ^{111}In and ^{201}Tl to mimic atom-at-a-time techniques. A variety of extractants have been studied, including ionic liquids, deep eutectic solvents, and low-transition-temperature mixtures. These compounds provide tunable properties, and a wide range of behavior has been observed. The results for ionic liquids typically show that Tl^{3+} is more easily extracted than Tl^{+}, but that an oxidizing agent is required. In^{3+} is typically only weakly extracted. Recent work has focused on developing new surfaces that could be used to measure the adsorption enthalpy of nihonium. An “offline” radiochemistry laboratory is available for these studies, as is an additional, smaller “online” laboratory. A recoil transfer chamber with good efficiency and fast extraction has been designed, fabricated, and characterized onsite, and is available for future studies. This talk will discuss the newest results of both offline and online experiments, and give an overview of the facilities that are available for chemical experiments.

NUCL 57

Studying the fundamental chemistry toward the end of the periodic table: The Heavy Element Chemistry program

***Philip Wilk**, pwilk-acs@zenspider.com. Basic Energy Sciences, United States Department of Energy, Germantown, Maryland, United States*

The elements beyond uranium were unknown before the Manhattan Project and since that defining moment, the Heavy Element Chemistry program has been continuously supported in some manifestation throughout the Atomic Energy Commission years up to the present-day Department of Energy due to its underlying support of DOE’s mission in Energy, Environment, and National Security. Knowledge of the chemical characteristics of the heavy elements under realistic conditions at liquid-solid and liquid-liquid interfaces is essential for the development of future nuclear fuel cycles. Fundamental understanding of the chemistry of these long-lived radioactive species is required to accurately predict and mitigate their transport and fate in the environment. Knowledge of the physical properties of defense-relevant elements is required to develop technologies to counter proliferation of weapon-useable nuclear material.

The role of 5*f* electrons in actinide bonds remains a fundamental topic in actinide chemistry; specifically, how they participate in the band structure of metallic and ceramic materials, and to what extent they participate in molecular actinide bond formation. Experimental validation of the theoretical properties of models will be the key to understanding the role of the 5*f* electrons. The heaviest elements are the elements that we know the least about. This is due partly to the challenges posed by doing chemistry with molecules containing radioactive isotopes, and partly due to the fact that most of these elements were not even discovered until recently. Research toward understanding the chemical bonding of elements that have 5*f* and 6*d* electrons will lead to a better quantum-mechanical understanding of all bonding, as molecules containing these elements at the extreme end of the periodic table pose an extreme test of our understanding of bonding.

NUCL 58

Reactor production of actinide materials for super-heavy element research

***David J. Dean**, deandj@ornl.gov, James Roberto. Oak Ridge National Lab, Oak Ridge, Tennessee, United States*

Bombardment of actinide target materials with ^{48}Ca beams has led to signficant advances in superheavy element research. Production of these actinide materials, including isotopes of Pu, Am, Cm, Bk, and Cf, requires highly specialized high-flux reactors and large-scale radiochemical processing facilities. Actinide materials from the High Flux Isotope Reactor and Radiochemical Engineering Development Center at Oak Ridge National Laboratory (ORNL) have been involved in the synthesis of nine superheavy elements, including nuclei with atomic numbers 104-106 and 113-118. We describe in this presentation the production and chemical processing of heavy actinide materials at ORNL and strategies for enhancing the production of rare actinides including ^{249}Bk. We review role of actinide materials in superheavy element research, including recent and ongoing experiments at the Joint Institute for Nuclear Reseach in Dubna, Russia using ^{239,240}Pu + ^{48}Ca to produce ^{284,285}Fl, the lightest isotopes of element 114 to date, and ^{251}Cf + ^{48}Ca to synthesize ^{296}118, which would be the heaviest nucleus ever made.

NUCL 59

TODGA-based solvent extraction system: An alternative to CLEANEX for Cf production

***Laetitia H. Delmau**, delmaulh@ornl.gov, Cory Dryman. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

N,N,N',N'-Tetraoctyl Diglycolamide (TODGA) is being evalutated as a promising solvent for curium-californium and other actinides separations with

the potentials of replacing HDEHP-based CLEANEX separation schemes. Preliminary experiments performed in our labs at Oak Ridge will be presented with discussions of future investigations.

NUCL 60

Heavy actinide complexation thermodynamics: Chemical signatures arising from limited materials

Jenifer Braley[1]*, jenifer.braley@gmail.com, Nathan Bessen*[1]*, Matthew Urban*[1]*, Ping Yang*[2]*. (1) Chemistry Geochemistry/Nuclear Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Heavy actinide chemistry is a notoriously difficult area to tread due to limitations in material availability and inherent radiation hazards. One means of making this chemistry more accessible is to couple thermodynamic measurements, that can be accomplished on the radiotracer scale, with computational studies that can aid in structural and electronic interpretation of thermodynamic data. Recent examinations of trans-curium actinide chemistry have observed covalency in actinide interactions can become more relevant with increasing atomic number. This presentation will consider the complexation thermodynamics for various ligands with the Cm through Es actinides to understand how the increased covalency in these systems could lead to changes in complex strength. Einsteinum investigations are of particular interest since Es stability constants only exist for approximately ten systems. Of these systems, Es complexation has been previously considered with relatively facile ligands such as hydroxide, chloride, sulfate, citric acid, 18-crown-6, etc. Changes in actinide complexation thermodynamics and computational modeling are then correlated to covalency signatures arising from other experimental techniques.

NUCL 61

Structural and thermodynamic considerations in the post-curium break

Thomas E. Albrecht-Schmitt*, talbrechtschmitt@gmail.com. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Recent experimental and computational investigations of a variety of berkelium and californium compounds have revealed a larger than expected

contraction in metal-ligand bond distances as well as a host of deviations from typical properties observed for actinides. The origin of these phenomena will be explained using a variety of spectroscopic and thermodynamic arguments. We will demonstrate that this break can be exploited for created chemistry not yet observed in lighter actinides.

NUCL 62

Single-ion manipulation in gas catchers and RF systems

***Guy Savard**, savard@anl.gov. Argonne National Laboratory and University of Chicago, Argonne, Illinois, United States*

Recent developments in the ability to isolate and manipulate rare single ions created by nuclear reactions offer great potential for the study of the atomic, chemical and decay properties of superheavy elements. The basic operating principles for single ion manipulation will be described and the technologies that have been developed to thermalize, capture and guide radioactive ions will be presented. The specific challenges to their application to superheavy element studies will be highlighted, together with possible measurements that these techniques will allow.

NUCL 63

Chemical studies of the transactinide elements

***Andreas Tuerler**[1,2], andreas.tuerler@psi.ch. (1) Chemistry and Biochemistry, University of Bern, Bern, Switzerland (2) Laboratory of Radiochemistry, Paul Scherrer Institute, Villigen PSI, Switzerland*

Investigation of superheavy elements is an exciting field of basic research in radiochemistry. The success of ^{48}Ca induced heavy ion fusion reactions on actinide targets has led to the synthesis of all elements up to atomic number 118 and the discovery of more than sixty new nuclides in the heavy element region over the past two decades. Thus, the 8th row of the Periodic Table has been completely filled. The attempted synthesis of elements 119 and 120 has failed so far. Experiments elucidating the chemical properties of heavy actinide and transactinide elements have made significant progress. Recently, the first ionization potential of lawrencium (Z=103) was experimentally determined in excellent agreement with advanced theoretical calculations, seaborgium (Z=106) was shown to form volatile hexacarbonyl complexes similar to its lighter homologs W and Mo, and, copernicium (Z=112) and flerovium (*Z*=114) showed an interesting, not yet conclusive behaviour that needs further clarification.

NUCL 64

High temperature uranium chemistry in condensing laser ablation plasmas

David Weisz[1]*, weiszdg@berkeley.edu, Jonathan C. Crowhurst*[1]*, Harry Radousky*[1]*, Timothy Rose*[1]*, Batikan Koroglu*[1]*, Wigbert Siekhaus*[1]*, Joseph M. Zaug*[1]*, Magdi Azer*[2]*, Mikhail Finko*[2]*, Davide Curreli*[2]*. (1) Lawrence Livermore National Laboratory, Livermore, California, United States (2) University of Illinois Urbana-Champaign, Champaign, Illinois, United States*

The processes that control vapor-phase radionuclide condensation and fractionation in near-surface nuclear fireball environments are poorly constrained . Determining the molecular form of vapor-phase radionuclides, such as uranium, will improve our understanding of post-detonation debris formation. Our goal is to quantify uranium oxide formation during low-temperature (~1 eV) plasma condensation . To do this, the time-resolved change in emission spectra from the laser ablation of uranium was observed in atmospheres having varying oxygen fugacities. We explored the effect of oxygen-isotope substitution on the emission spectrum of uranium using ^{18}O-enriched gas to positively identify UO emission features. To generate plasma conditions, a 1064 nm Nd:YAG was used to ablate uranium metal with 5 ns pulses. These data provide insight into the formation conditions of uranium oxide species (including UO) during plasma condensation, and will serve as input parameters to a kinetics-based, semi-empirical computational model that describes gas phase uranium oxide chemistry.

NUCL 65

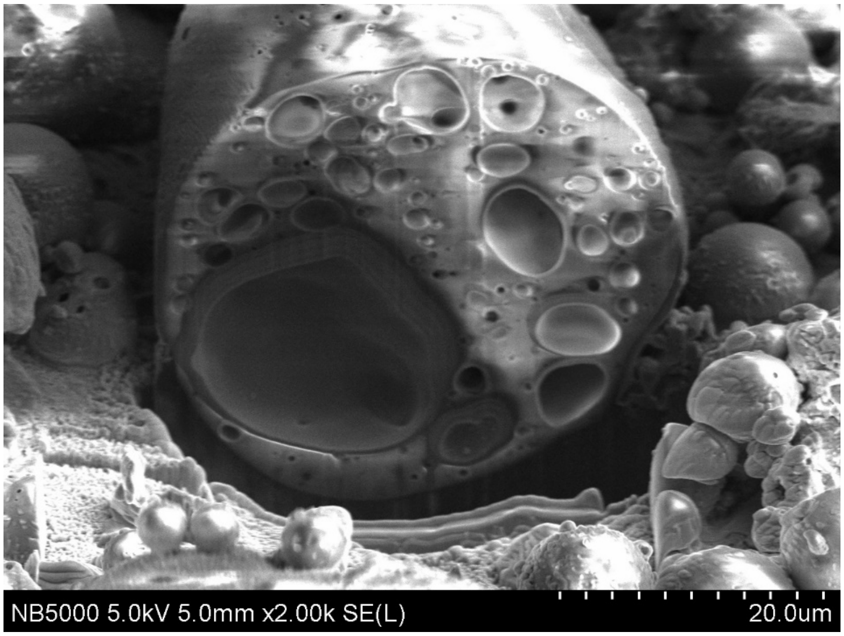
Preparation of surrogate post-detonation debris using a plasma torch

***Paul A. Taylor**, taylorpa@ornl.gov. Process Engineering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

A commercial plasma spray system is being used to prepare powders that have been exposed to the extremely high temperatures present in a plasma torch (10,000–15,000°C). The feed powders represent materials present at the Trinity site in New Mexico and at selected urban sites[1]. The goal of the project is to provide the surrogate debris for analyses such as particle

dispersion and leaching rates. The primary constituents of the Trinity composition are silica (~60 wt%) and alumina (~14 wt%), with smaller amounts of calcium oxide (~9 wt%), potassium oxide (~6 wt%), sodium oxide (~2 wt%) and magnesium oxide (~2 wt%). The urban feeds have a similar compositon with an iron concentration of about 10% and then trace amounts of many other metals. The powder feeder for the plasma gun can handle particle sizes ranging from 20–200 µm, but a narrow particle size distribution is desired to ensure that the particles are uniformly exposed to the plasma arc. A laser-based particle visualization system is used to show the path of the particles into the plasma arc. The flow rate of the carrier gas can be adjusted to optimize the exposure of the particles to the arc. The average surface temperature of the particles as they leave the plasma arc is being measured. A spray dryer is used to produce composite particles of the desired composition, using small amounts of an organic binder.

Plasma gum running with 9% hydrogen in argon



SEM image of melted particles

NUCL 66

High temperature aging study of UO_2 and U_3O_8 for nuclear forensics

Adam M. Olsen[2], *adam.olsen@utah.edu, Luther W. McDonald*[1]. *(1) The University of Utah, Salt Lake City, Utah, United States (2) Civil Engineering, University of Utah, Salt Lake City, Utah, United States*

Morphological particle analysis of interdicted nuclear material is a promising new area of nuclear forensic science. Quantifying morphological changes in uranium oxides enables these physical features to serve as a signature of the materials processing history. In this study, the impact of temperature and partial pressure of O_2 on the morphology of UO_2 and U_3O_8 was evaluated. A response surface design of experiment (DOE) model was developed to enable statistical comparison between the parameters of interest. Following synthesis, the purity of each sample was determined by powder X-ray diffraction (XRD). Brunauer-Emmett-Teller method (BET) was used to monitor changes in the specific surface area (SSA); while scanning electron microscopy (SEM) was used to monitor morphological features. These features were segmented using the Morphological Analysis for MAterials (MAMA) software enabling statistical analysis of the resulting data. Results demonstrating the morphological signatures of UO_2 and U_3O_8 as they are

aged will be discussed to reveal their use as another valuable tool for nuclear forensic analysis.

NUCL 67

Quantitative morphological analysis of actinide materials

Kristi L. Pellegrini[2]*, kristi.lynn.66@gmail.com, Jennifer A. Soltis*[2]*, Edgar Buck*[2]*, Lucas Sweet*[2]*, David E. Meier*[1]*. (1) P7-25, Pacific Northwest National Lab, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States*

Electron microscopy of actinide materials has been implemented since as early as the 1950's and has provided a great deal of information about the morphology of a variety of materials from a qualitative standpoint. The limit of qualitative morphological analysis is in the bias of a particular observer—where one person may see differences between samples, another may not. The goal of probing morphology of samples is not to solely ask the question "Do these samples look different?", but to quantify the difference in particular parameters in an image and then numerically distinguish samples from each other. Here we present the quantitative morphological analysis of scanning electron microscopy (SEM) images of multiple actinide materials using the MAMA software developed at Los Alamos National Laboratory. Samples of actinide materials were imaged using SEM, and the MAMA software was used to segment the images and perform quantitative analysis of several particle attributes, which include information about the particle area and diameter, as well as circularity of the particles. The MAMA output was then used to create histograms for each sample and determine the change in histograms as a function of the number of particles imaged per sample. We also discuss the added difficulty of analyzing complex samples with multiple populations.

NUCL 68

Dependence of UO_2 surface morphology on synthesis route

Erik Abbott[2]*, u1084814@utah.edu, Luther W. McDonald*[1]*. (1) The Univ of Utah, Salt Lake City, Utah, United States (2) Nuclear Engineering, University of Utah, Salt Lake City, Utah, United States*

Surface morphology of uranium oxides is a defining characteristic of the of the processing history of the material. Since UO_3 and U_3O_8 are common materials for production of UO_2, amorphous UO_3, alpha-UO_3, and U_3O_8 were reduced to

UO_2 in hydrogen at 510 °C to show that the unique differences in surface morphology of the resulting UO_2 are caused by the differences in the parent materials. The resulting UO_2 and parent materials were analyzed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller method (BET), and particle X-ray diffraction (XRD). SEM was used to monitor changes in the morphology; while BET was used to monitor changes to the specific surface area. XRD and XPS were used to verify the purity of the final product. The Morphological Analysis for MAterials (MAMA) software was used to segment the SEM images and quantify the morphological changes. Results will be shown highlighting the quantifiable differences in the UO_2 surface structure and morphology based on the starting material.

NUCL 69

Three-dimensional morphological signatures for nuclear forensics

Brandon Chung, *chung7@llnl.gov, David Roberts, William Talbot, Denise Ashley, Nick Teslich. Lawrence Livermore National Laboratory, Livermore, California, United States*

Nuclear forensics requires accurate identification of distinguishing characteristics and provenance of interdicted nuclear materials. Nuclear materials can contain unique morphological features from their production processes and exposure to changing environments. In this study, we present our current effort to accurately quantify discriminating morphological characteristics of the bulk uranium and plutonium metals. We will discuss advantages of our approach using focused ion beam techniques to extract forensic signatures that are entrapped within the bulk metal and its subsurface oxide scale. Our work will show that the three-dimensional (3D) characterization of the interior of the bulk nuclear material provides higher-fidelity morphological features than conventional two-dimensional (2D) morphological characterization methods. These 3D features are forensics signatures revealing the production history tied to the chemical and metallurgical processes. We will also present our recent effort to investigate material signatures entrapped within the bulk, subsurface oxide scale formed over the plutonium metal for the recent provenance of nuclear materials.

NUCL 70

Impact of controlled storage conditions on the hydration and morphology of UO3

***Ian Schwerdt**, ischwerdt152@gmail.com, Luther W. McDonald. Civil and Environmental Engineering, University of Utah, Bluffdale, Utah, United States*

Traditional nuclear forensic analysis techniques currently have a limited capability to determine the historical storage conditions of interdicted materials. A material of interest, uranium trioxide, is known to react with atmospheric moisture to form several hydrated species. The speciation and extent of hydrate formation is primarily dependent on the storage temperature, exposure time, and relative humidity of the sample’s environment. In this application, the morphological and microstructural properties of amorphous-UO3, under controlled storage conditions, are being investigated using powder X-ray diffraction (p-XRD) and scanning electron microscopy (SEM). These techniques are being utilized to identify quantitative signatures that are indicative of the storage process history for UO3 samples. The high-resolution SEM images acquired are statistically compared using Morphological Analysis for Material Attribution (MAMA) software developed at Los Alamos National Laboratory. Quantitative XRD will be utilized to determine the composition of the hydrated UO3 samples. The utility of the surface morphology and microstructure for assessing process history cannot be realized without a fundamental understanding of the impact of post-synthesis storage conditions. In this study, high-purity amorphous-UO3 is synthesized from the thermal decomposition of uranyl peroxide. Additionally, saturated salt solutions are employed to maintain controlled relative humidities in the storage vessels over the course of the study. The impact of the storage temperature and relative humidity over time will be statistically evaluated as potential sources of morphological variation utilizing the generation of a statistically rigorous multivariate response surface model.

NUCL 71

Multi-variate statistical analysis enhancing preliminary morphological signature development strategies for nuclear forensic-related materials

***Ashton D. Lesiak**, alesiak@lanl.gov. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

There is an increasing need in forensics as a whole for quantitative methodologies capable of driving legally defensible data interpretations. In our efforts, initial studies on morphology analysis of nuclear materials, using the morphological analysis for materials (MAMA) software package developed at LANL, has provided preliminary quantitation of particle features measured in scanning electron microscopy images and is here, for the first time, combined

with other parameters from material characterization (e.g. trace elements, isotopics, etc.) to facilitate multi-variate statistical analysis/differentiation. Five uranium oxides from two international round robin studies were analyzed for full chemistry and three of those samples were further subjected to morphological analysis via MAMA processing. Statistical processing, using Eigenvector Research Solo Software (commercial, off the shelf software), was performed, using (1) trace element and isotopic measurements, (2) independent MAMA morphology values, and (3) a combined approach incorporating both of these former data sets simultaneously. Principal components analysis indicated that samples from the two round robin studies could be distinguished by chemistry data alone, however the multiple samples within each study overlapped. Single particle analysis from MAMA was less effective at providing separation between samples, but averaged values were able to resolve the round robin studies. When combined with the MAMA morphology data, the three individual samples could be resolved from one another within a 95% confidence level. The initial success of the statistical analysis processing of uranium oxides indicates that using principal components analysis, along with other techniques such as hierarchical clustering analysis and partial least squares discriminant analysis can distinguish nuclear materials based on their chemical and morphological signatures and may provide context for manufacturer or origin of the material in question.
This abstract is LA-UR-17-23272.

NUCL 72

NNSA Graduate Fellowship Program experience

April Gillens, *april.gillens@nnsa.doe.gov. National Nuclear Security Administration, Washington, District of Columbia, United States*

The National Nuclear Security Administration (NNSA) is a semi-autonomous agency in the Department of Energy (DOE) responsible for providing the United States with a safe, secure, and effective nuclear stockpile. The NNSA Graduate Fellowship Program (NGFP) is an opportunity to gain professional experience at DOE Headquarters (HQ) in support of the national security enterprise. The NGFP is open to graduate students pursuing technical and/or policy degrees in nuclear related fields as well as post-doctoral and post-master candidates. The NGFP exposes participants to high level processes at HQ and at field offices that support the DOE national laboratories. Fellows will gain experience across multiple platforms that sustain the national security enterprise including the federal budget process, acquisition of funds to support

science, operations, and maintenance at the DOE national laboratories, and program management. Fellows will also receive specific training in weapons physics and diagnostics as well as other specialized training. This presentation will give students an insight on the benefits of the fellowship program and how the skills obtained are transferrable to technical and managerial positions within the weapons complex. I have participated in the Class of 2016 NGFP and have completed the program as of June 2017.

NUCL 73

Detailed *in-situ* chemical characterization and Pb-Pb age dating of uraninite from North American deposits

Stefanie Lewis[2], *stefanie.lewis08@gmail.com, Loretta Corcoran*[3]*, Antonio Simonetti*[4]*, Peter C. Burns*[1]*. (1) Univ of Notre Dame, Notre Dame, Indiana, United States (2) University of Notre Dame, South Bend, Indiana, United States (3) CEEES, University of Notre Dame, Notre Dame, Indiana, United States (4) Dept. Civil Enviro Eng Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Chemical heterogeneity of natural uraninite from North America deposits is currently under investigation using a variety of *in situ* analyses for nuclear forensic applications. Analyses include quantifying rare earth element (REE) abundances, and the concentrations and isotopic composition of Pb for provenance and geochronology purposes. Furthermore, trace element distributions in Pb-rich regions (15-20 wt%) are compared to those of Pb-poor areas (<10 wt%) so as to investigate the mobility of elements incompatible within the uraninite structure. X-ray fluorescence (XRF) chemical mapping was used to determine qualitative elemental distribution and spatial information, and electron microprobe analysis (EMP) was employed for spatially resolved quantitative chemical analyses. Trace element distributions were determined using high spatial resolution laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS), whereas Pb isotope compositions were obtained by LA-multicollector-ICP-MS. Trace element analyses enabled the comparison of forensic signatures between Pb-rich and Pb-poor U phases, which can be associated with temperature, host rock composition, fluid salinity, and REE availability of the geological setting.

NUCL 74

Atomistic insight into phase formation and alteration of uranium phases

***Lindsay C. Shuller-Nickles**, lshulle@clemson.edu. Clemson University, Anderson, South Carolina, United States*

Atomistic scale calculations are being used to determine the underlying chemical controls on uranium phase formation and alteration. The national and international nuclear forensic community aims at relating microstructural information with materials process history. However, the breadth of experiments and analysis necessary to develop a comprehensive list would be overwhelming. The fundamental chemistry governing phase formation and alteration can be probed at an atomistic scale using quantum-mechanical calculations. Observation and quantification of energetics and changes to electron density enable a predictive understanding of the fundamental chemistry controlling the presentation of actinide oxide phases. For example, the relationship of the surface energies of a uranium alteration phase can indicate the crystal form of the bulk phase. In this work, the (100), (110), (001), and (111) surfaces of coffinite ($USiO_4$) were computed showing that, like zircon ($ZrSiO_4$) the (100) face has the lowest surface energy. While zircon can form large euhedral crystals, coffinite tends to form more anhedral crystals. The range of the evaluated surface energies of coffinite (ranging from 0.67 J/m^2 to 1.29 J/m^2) is an indication that large euhedral crystals are unlikely to form, as compared with the range in surface energies for the same surfaces of zircon (0.88 J/m^2 to 3.68 J/m^2). Another example of atomistic scale investigations for nuclear forensics applications is the incorporation of a dopant into a uranium oxide system. Divalent cations may be present in the formation of uranium dioxide as an impurity in a processing facility (e.g., Ca remnant from U-metal and oxide processing), as a fission product remaining in a used fuel (e.g., Sr in used UO_2 fuel), or as a daughter product in natural uranium (e.g., Pb in natural UO_2). The incorporation mechanism of divalent cations into UO_2 is not confirmed, but may occur via oxidation of U^{4+} to U^{6+}. Here, density functional theory calculations were used to quantify the incorporation mechanism and confirm the association of uranium oxidation with divalent cation incorporation.

NUCL 75

Deposit type average rare earth element signatures for nuclear forensics

***Tyler L. Spano**[2], tspanofr@nd.edu, Antonio Simonetti[2], Grace Carpenter[2], Devonee Freet[2], Enrica Balboni[2,3], Thomas Wheeler[2], Corinne Dorais[2], Peter C. Burns[1]. (1) Univ of Notre Dame, Notre Dame, Indiana, United States (2) Dept. Civil Enviro Eng Earth Sciences, University of Notre Dame, Notre*

Dame, Indiana, United States (3) Lawrence Livermore National Laboratory, Livermore, California, United States

Provenance determination for uranium-rich materials is a critical objective of nuclear forensic analysis. Rare earth element (REE) distributions within uranium ores have seen extensive use as forensic indicators, but quantifying and correlating trace element signatures for U ores to known deposits has thus far involved intricate statistical analyses. Average chondrite normalized (CN)-REE signatures for important U deposit types (DT) worldwide have been calculated and employed to evaluate U ore paragenesis using a simple linear regression analysis. Average DT-CN-REE signatures for unconformity-related, vein type, sandstone, intrusive, and metamorphic type U deposits were established. Uranium ores and derivative materials (uranium ore concentrate) of known origins were treated as unknowns, and in all cases the deposit type from which the sample originated could be positively identified using this method. This novel technique provides a means for rapid assessment of the deposit type of U ores based on their REE abundances.

NUCL 76

Chemical characterization of altered and unaltered uraninites from various geological settings

***Loretta Corcoran**[3], lcorcora@nd.edu, Antonio Simonetti[4], Tyler L. Spano[3], Stefanie Lewis[2], Peter C. Burns[1]. (1) Univ of Notre Dame, Notre Dame, Indiana, United States (2) University of Notre Dame, South Bend, Indiana, United States (3) CEEES, University of Notre Dame, Notre Dame, Indiana, United States (4) Dept. Civil Enviro Eng Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

The major and trace element concentrations of a global suite of unaltered uraninite samples from five distinct deposit types; sandstone, intrusive, unconformity, vein, and metamorphic have been characterized. The spatial distribution and concentrations of major and trace elements (U, Pb, Th, Al, As, Ca, Fe, K, Mn, P, Si, S, Ti, V, Y, and Zr) were qualitatively determined by X-ray fluorescence (XRF) and subsequently quantified by electron microprobe analysis (EMP). The concentration of rare earth elements (REEs) and other trace elements, which are potentially significant depending on the deposit type (e.g. W, Bi, and Mo) were examined by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). Following the chemical fingerprinting of the unaltered uraninite samples, a set of altered uraninites from the same locations were analyzed employing the same methods. The

comparison of altered and unaltered uraninites from the same location allows for the evaluation of major and trace element mobility under various environmental conditions, such as oxidation state, over geological time. This study may provide valuable insights into the potential behavior of elements during the aging and corrosion of uranium oxide concentrate in nuclear fuel pellets and hence applicable for nuclear forensic investigations.

NUCL 77

Novel dissolution chemistry for post detonation nuclear debris

John D. Brockman[3]*, brockmanjd@missouri.edu, Nicholas T. Hubley*[2]*, Christian Mason*[3]*, Dana Wegge*[2]*, John D. Robertson*[1,3]*. (1) Univ of Missouri, Columbia, Missouri, United States (2) Chemistry, University of Missouri, Columbia, Missouri, United States (3) Research Reactor, University of Missouri, Columbia, Missouri, United States*

Rapid dissolution methods for nuclear detonation debris analysis are needed to facilitate rapid analysis of key radioisotopes. Current best practice uses a combination of nitric acid and hydrofluoric acid with heat at atmospheric pressure or in pressure vessels. In this work, we evaluate three methods for rapid dissolution of surrogate nuclear debris; sonication assisted dissolution with HNO_3 and ammonium bifluoride, fusion with ammonium bifluoride, and fusion with lithium metaborate. Ammonium bifluoride is a fluorinating agent used to produce in-situ HF. In the sonication dissolution method, the samples are reacted with ammonium bifluoride and HNO_3 in polypropylene tubes. The sample tubes are placed near an indirect sonication horn operated at 800 W and maintained at 55 °C using a chiller. The method resulted in quantitative elemental recoveries for USGS reference materials DNC-1a Dolerite, QLO-1a Quartz Latite, SDC-1 Mica Schist, and BHVO-2 Hawaiian Basalt, while recovery of elements in USGS AGV-2 Andesite and NIST SRM 278 Obsidian and 1413 High Alumina Sand were low. Dissolution by fusion of a sample with ammonium bifluroride at temperature of 230 °C or greater will be presented for gram sized samples using 60 mL PFA tubes and Pt crucibles. Finally, the recovery of fission products following sample fusion with lithium metaborate at 900 °C will be reported.

NUCL 78

Extraction of cesium ion with dibenzo-18-crown-6 from aqueous solutions using organic solvents

***Rima Biswas**[2], biswasrima622@gmail.com, Tamal Banerjee[3], Pallab Ghosh[1], Sk. Musharaf Ali[4]. (1) Chemical Engineering, IIT Guwahati, Assam, Assam, India (2) Chemical Engineering, IIT Guwahati, Guwahati, Assam, India (4) Chemical Engineering Division, Bhabha Atomic Research Center, Mumbai, Maharashtra, India*

Extraction of cesium ions in presence of ionophore such as dibenzo-18-crown-6 (DB18C6) from organic solvents (i.e chloroform, nitrobenzene, and octanol)-water biphasic system is reported by COSMO-RS (Conductor like Screening Model for Real Solvents) and Molecular dynamics (MD) simulation. High value of selectivity of Cs^+-DB18C6 complex was obtained for nitrobenzene (7.03) at 308.15 K. It indicates an excellent extraction efficiency of nitrobenzene for Cs^+ ion in presence of DB18C6. Thereafter to understand the mechanism of complexation and the behavior of crown ether ligand, we simulated 10 $Cs^+NO_3^-$ ion pairs and 10 DB18C6 at the preformed organic solvents-water interface. It was observed that the Cs^+–DB18C6 complex formed during the simulation diffused at a slower rate as compared to other free species from the interface to bulk IL phase. The radial distribution function (RDF), free energies ,interaction energies and the diffusion coefficient during complexation of Cs^+ with DB18C6 were also computed.

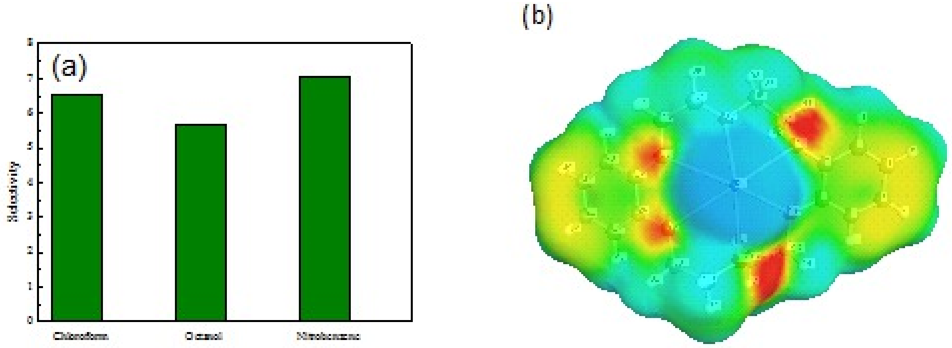


Figure 1. (a) Selectivity of Cs^+-DB18C6 complex in chloroform, octanol and nitrobenzene at 303K. (b) COSMO segmented surface of Cs^+-DB18C6 complex

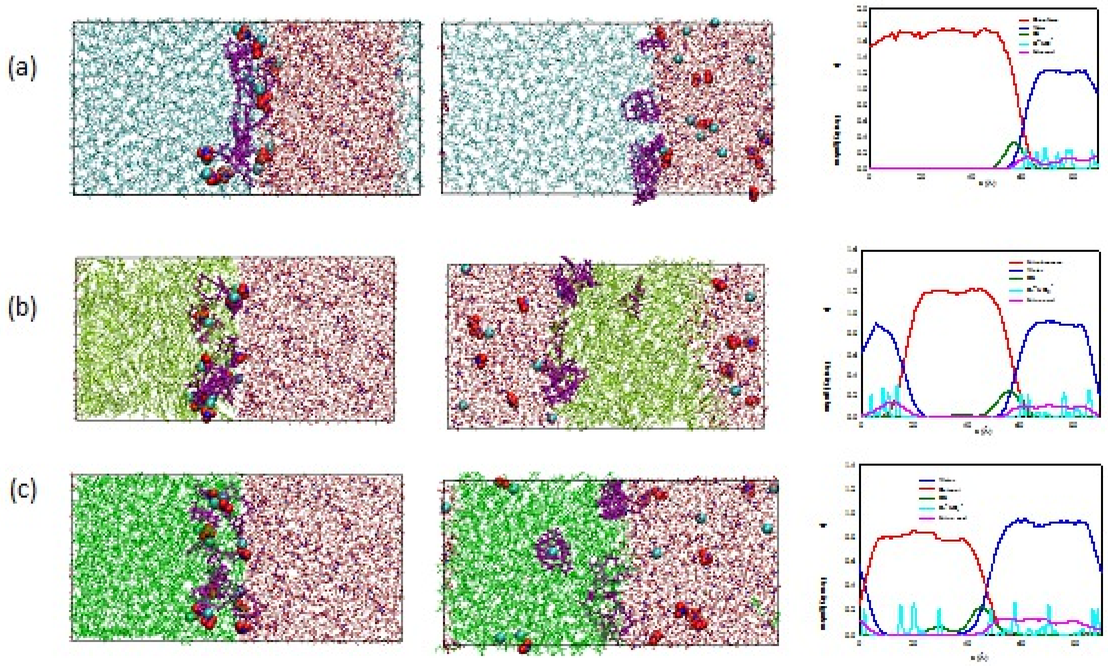


Figure 2. Initial and final snapshots of (a) chloroform (*cyan*)-water (*red*) (b) nitrobenzene (*lime*)-water (*red*) (c) octanol (*green*)-water (*red*) systems with Cs$^+$NO$_3^-$(*cyan*). Plots for density are affixed to the right side.

NUCL 79

Oxygen isotope fractionation in the processing of uranium oxides relevant to the nuclear fuel cycle

Michael R. Klosterman[2]*, michael.klosterman@utah.edu, Luther W. McDonald*[1]*. (1) The Univ of Utah, Salt Lake City, Utah, United States (2) Civil & Environmental Engineering, University of Utah, Salt Lake City, Utah, United States*

Oxygen isotope ratios of uranium oxides are known to correlate with those of the fluids from which they precipitated. The variety of processing routes utilized in the nuclear fuel cycle, from ore concentration through enrichment, will therefore contribute to a wide variation in $\delta^{18}O$ values encountered among uranium oxides. Application of this information for nuclear forensics purposes requires an understanding of the oxygen isotopic fractionation induced through certain processing conditions. The initial focus of this study is an interrogation of changes in the $^{18}O/^{16}O$ ratio along each step of commonly employed synthetic routes, with variation in the chemical compositions of starting materials. Beginning with a uranyl nitrate starting material depleted in ^{18}O, uranium oxide intermediate products—uranyl nitrate, uranyl peroxide,

or ammonium diuranate—were synthesized and/or precipitated from aqueous solutions enriched in ^{18}O. Each of these compounds was then calcined to a final product of uranium trioxide or triuranium octoxide. Identification of each uranium species was confirmed using powder X-ray diffraction (XRD), while oxygen isotope ratios of the starting materials and their corresponding products were measured using both a High Vacuum Fluorination System (HVFS) coupled with Isotope Ratio Mass Spectrometry (IRMS) and Secondary Ion Mass Spectrometry (SIMS). Results of oxygen isotope fractionation arising from variation in processing methods will be discussed, along with their implications for future nuclear forensic investigations.

NUCL 80

Phase-field modeling of the U,C-UC liquid-solid interface for the formation of UC microstructures

David Abrecht, *david.abrecht@pnnl.gov. Pacific Northwest National Laboratory, Richland, Washington, United States*

The shape and structure of secondary phase inclusions and their development over time can provide valuable information as to the history of a material and the conditions under which the material was formed. Cast uranium metal typically contains a number of “angular inclusions” consisting of carbide and oxide impurities present in the melt that grow and develop while the molten phase is present due to the continuous introduction of impurities and the thermal mixing in the cast. To better understand this formation process and the dependence of the process on the production conditions in the melt, phase-field models are being developed to investigate the effects of temperature and carbon concentration on the dynamic size and shape of uranium monocarbide (UC) particles as they grow from the molten uranium. In this discussion, we present current progress on the development of the models and directions for additional features and further model development.

NUCL 81

Chemist’s stint with nuclear forensics at the State Department

Christopher L. Cahill, *cahill@gwu.edu. George Washington Univ, Washington, District of Columbia, United States*

This presentation will describe the evolution of interests of an academic, PhD chemist as he explored an ‘alternative’ career path in the government. Prof.

Cahill took a one year sabbatical from his faculty position at The George Washington University and, through the American Institute of Physics' State Department Science Fellowship, spent a year in the Bureau of International Security and Nonproliferation's Office of Weapons of Mass Destruction-Terrorism. This experience provided him with some keen insight for those wishing to explore careers in the government, federal agencies, or other forums at the intersection of science ad technology policy. As such, he will present a brief overview of his path to the position, his experiences therein, and hopefully foster an open discussion regarding opportunities and suggestions for engagement.

NUCL 82

Age dating of Sr-90 using DGA resin

***Derek McLain**, mclaindr@anl.gov. Argonne National Laboratory, Lemont, Illinois, United States*

While the consequences of an attack utilizing a radiation dispersal device (RDD) would not be nearly as severe as those associated with an Improvised Nuclear Device (IND), the likelihood of an RDD attack by a terrorist organization is much higher. Because of this, there has been an effort to develop methods for age-dating radiological sealed sources in recent years. One such procedure, developed by Argonne National Laboratory, is used for determining the age of Sr-90 sources. Unfortunately, the procedure utilizes a rather expensive extraction chromatography resin and requires all measurement instrumentation to support radioactive material. The work presented investigates using an alternative separation scheme that not only utilizes a less costly resin, but also results in the isolation of Sr-90's stable granddaughter, Zr-90. This allows the strontium quantification to be done radiometrically and removes the requirement for an ICP-MS that has seen radioactive material for zirconium quantification, increasing the number of instruments capable of making the measurement and making high throughput of samples much simpler.

NUCL 83

Development of a Cs-Ba radiochronometry reference material for nuclear forensics

***Kevin B. Lavelle**[1], kevin.lavelle@nist.gov, Kevin P. Carney[2], Jeffrey T. Cessna[1], Richard M. Essex[1], Cole R. Hexel[3]. (1) National Institute of*

Standards and Technology, Gaithersburg, Maryland, United States (2) Idaho National Laboratory, Idaho Falls, Idaho, United States (3) Oak Ridge National Laboratory, Knoxville, Tennessee, United States

A reference material for age dating of ^{137}Cs sealed source material has been produced and characterization of this material for key attributes has been completed. ^{137}Cs is one of the radionuclides most commonly used in sealed radioactive sources produced for a wide variety of medical and industrial applications. Several incidents have been documented in which sealed ^{137}Cs sources were lost or stolen including a significant contamination event associated with an abandoned source in Goiânia, Brazil in 1987, theft of a source in Estonia in 1994, and loss of a source in Honduras in 2010. These incidents suggest that a sealed ^{137}Cs source could potentially be the subject of a future nuclear forensic investigation. A useful signature for identifying the provenance of ^{137}Cs source material is the model purification age, which represents the last time at which ^{137}Cs was separated from its decay product, ^{137}Ba. For this reason, the Department of Homeland Security's Domestic Nuclear Detection Office (DNDO) has sponsored production a reference material for ^{137}Cs-^{137}Ba radiochronometry. 200 units of a Cs-Ba radiochronometric reference material were created by encapsulating 5 mL of a ^{137}Cs master solution in quartz glass ampoules. The master solution was created from a small quantity of CsCl that was obtained from a 20 Ci ^{137}Cs sealed source previously opened for examination. Measurements were performed on selected units of the reference material to determine values for amount content of ^{137}Cs and radiogenic ^{137}Ba (referred to as ^{137}Ba*) and a model purification date. The activity of ^{137}Cs was measured using the NIST 4π-γ reentrant ionization chamber "A" at 348.4 ± 3.0 ($k = 2$) kBq/g and was converted to an amount content of 0.791 ± 0.008 ($k = 2$) nmol/g using the ^{137}Cs half-life; independent measurements by isotope dilution mass spectrometry (IDMS) verify this result. The ^{137}Ba* concentration of 1.551 ± 0.021 ($k = 2$) nmol/g was also determined by IDMS and verified by independent IDMS measurements at a second laboratory. Prior to determination of concentration by isotope dilution mass spectrometry, isobaric ^{137}Cs and ^{137}Ba were separated by gas pressurized extraction chromatography using Eichrom's Sr resin. The measured ^{137}Cs and ^{137}Ba* indicate a model purification date of June 16, 1964 ± 190 ($k = 2$) days. This date is over 1 year prior to the known encapsulation date of October 27, 1965 and is, therefore, consistent with the history of this source.

NUCL 84

Gas chemical adsorption characterization of lanthanide chelates

***Steven Stratz**[2], adamstratz@yahoo.com, Howard Hall[2], John D. Auxier[1]. (1) Department of Nuclear Engineering, Institute for Nuclear Security, Jefferson City, Tennessee, United States (2) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States*

Thermodynamic adsorption characteristics of twelve lanthanide hexafluoroacetylacetoneates have been measured for the first time. The deposition temperature along a capillary column in a thermochromatographic system was used in a variety of pressure environments to converge adsorptive behavior of these complexes. Resulting adsorption enthalpies were used in thermodynamic and Monte Carlo simulations to attempt to optimize a large-scale gas-phase separation experiment of the twelve complexes. Results of these models and their pertinence to nuclear forensic analysis is discussed.

NUCL 85

New K-edge densitometry calibration technique

***Michael D. Yoho**[1], myoho@lanl.gov, Duc T. Vo[2], Donivan R. Porterfield[1]. (1) Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Safeguards Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Hybrid K-edge/XRF densitometry (HKED) is an important nondestructive assay method for determining the concentrations of special nuclear materials in solutions. HKED is widely used for safeguarding reprocessing plants and for determining the uranium and plutonium content in nuclear forensics samples. The current calibration method for K-edge densitometry does not take into account small-angle Compton scattering. A new calibration method will be presented which takes this scattering into account. The new method reduces the time and money spent on system calibration, reduces systematic error, and eliminates the need for recalibration after the degradation of the x-ray tube tungsten target. The method will be derived and validated with experimental data. Further, the elimination of the dependency between calibration accuracy and tungsten target integrity will be verified by modelling.

NUCL 86

FBI nuclear forensics

***James Blankenship**, James.Blankenship@ic.fbi.gov. FBI, Quantico, Virginia, United States*

Dr. James Blankenship is a forensic examiner with the Federal Bureau of Investigation (FBI) at the FBI Laboratory in Quantico, Virginia. His work with the laboratory is focused on leading the analysis of weapons of mass destruction, including nuclear and radioactive dispersal devices. Previously, Dr. Blankenship has been an executive officer in the Pentagon, supported the assistant to the Secretary of Defense for nuclear and chemical and biological defense programs, and has served as a program manager to the Defense Threat Reduction Agency. Dr. Blankenship received his PhD in chemistry from Texas A&M university. Dr. Blankenship will be presenting on his work with nuclear forensics.

NUCL 87

Nuclear Forensics International Technical Working Group collaborative materials exercises: Advancing the state and practice of nuclear forensic analysis since 1999

***Jon M. Schwantes**, Jon.schwantes@pnnl.gov. Pacific Northwest National Laboratory, Richland, Washington, United States*

The Nuclear Forensics International Technical Working Group (ITWG) is a forum for informal collaboration among official nuclear forensics practitioners affiliated with national government programs and sharing a common interest in preventing illicit trafficking of nuclear and radioactive materials out of regulatory control. Together, this community of scientists, law enforcement personnel, and regulators work to advance the best practices of nuclear forensics largely through the participation in a series of Collaborative Materials Exercises (CMXs). This presentation will discuss the advancement of the science and state of practice of nuclear forensic analysis over the 18-year history of ITWG and its CMX’s.

NUCL 88

Software and analysis methods for the determination of americium in plutonium via alpha spectrometry

***Michael D. Yoho**, myoho@lanl.gov, Donivan R. Porterfield, Jung Rim. Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

The in-growth of ^{241}Am from the decay of ^{241}Pu is a well-regarded chronometer for the determination of the time since last chemical-separation in plutonium-based nuclear forensics samples. Alpha-spectrometry software will be presented that determines the relative amount of ^{241}Am in plutonium special nuclear material with about a 1% (k = 2) total uncertainty. This is achieved by incorporating Pu isotopics determined by thermal ionization mass-spectrometry into the analysis and by utilizing accurate conversion-electron and tailing functions. Due to the lack of a consensus americium in bulk plutonium standard, it is difficult to determine overall measurement bias. Therefore, a total measurement uncertainty is determined by a GUM (Guide to the Expression of Uncertainty in Measurement) bottom-up methodology. Sources of uncertainty include Poisson statistics, nuclear data, deconvolution, interferences and sample inhomogeneities.