NUCL 1

Predictive practical approaches to heavy-element computational chemistry for nuclear security

Robert J. Harrison[1]*, rjharrison@gmail.com, Deborah A. Penchoff*[2]*, Howard L. Hall*[3]*. (1) Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York, United States (2) , Institute for Nuclear Security, Knoxville, Tennessee, United States (3) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States*

A collaboration between the Institute for Nuclear Security (INS) at the University of Tennessee and the Institute for Advanced Computational Science (AICS) at Stony Brook University is tightly integrating computational science with the experimental chemistry program at INS that is focused upon advancing nuclear security. In the talk we will review some of the ongoing activities and initial results. We will also discuss paths to fast and robust computation by replacing atomic basis sets with numerical representations with guaranteed accuracy and speed.

NUCL 2

Separation of americium-241 and plutonium-238

John Auxier*, jauxier@utk.edu. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

We are currently pursuing the development of a new method for the detn. of plutonium and americium-241 at elevated levels in process aq. samples. The main objective of this new method is to reduce the usage of hazardous chems. At the same time we also wish to at least maintain comparable accuracy and precision characteristics with any new method. As well sample turn-around is an important consideration. The new method being pursued would utilize gas proportional counting for total alpha activity and alpha spectrometry for the relative amts. of plutonium and americium-241 in a dild. sample aliquot. We anticipate also utilizing typical plutonium isotopic abundance information to correct for the contribution of plutonium-238 to the americium-241 alpha spectrometry region-of-interest. While there is good sepn. between the major plutonium alpha emissions and that of americium-241 and plutonium-238 some correction for alpha spectrometry peak tailing is expected to be necessary.

NUCL 3

Coupled cluster studies of actinyl interactions in the gas phase

*Rulin Feng, **Kirk A. Peterson**, kipeters@wsu.edu. Washington State University, Pullman, Washington, United States*

Using the coupled cluster CCSD(T) method in conjunction with sequences of all-electron correlation consistent basis sets and the 3rd-order Douglas-Kroll-Hess relativistic Hamiltonian, accurate energetics are reported for a variety of fundamental actinyl (AnO_2^{n+}) interactions in the gas phase. These range from actinyl-actinyl dimer complexes, so-called cation-cation interactions, where the actinides range from An=U to Am, to the binding of small molecules like N_2 and CO to individual actinyls with An = U and Np. Variations of the Feller-Peterson-Dixon (FPD) composite method is used throughout. While the cation-cation complexes are very thermodynamically unstable in the gas phase due to the strong coulombic repulsion, many possess what are presumably kinetically stable minima with calculated well depths behind a coulombic barrier ranging up to -15 kcal/mol. Natural bond orbital analyses indicate that the interaction is due to short-range charge transfer from an sp-hybridized lone pair on the oxygen of the donor actinyl to a vacant sdf-hybridized valence orbital of the acceptor An atom. For (AnO_2^+)-(AnO_2^+) complexes, the calculated well depths decrease in magnitude from U to Am. The trends are consistent with observations in condensed phases. Two bonding motifs were investigated for the interaction of N_2 and CO with AnO_2^{n+}(n=0-2). Both end-on (η^1) and side-on (η^2) minima were found for the neutral complexes, while only the η^1 complexes were calculated for the cations. The N-N and C-O bonds were found to be activated for η^2 complexes, with vibrational frequencies of N_2/CO red-shifted by as much as 480 cm^{-1} with a corresponding 0.06 Å bond length elongation.

NUCL 4

Understanding selectivity of lanthanide and actinide compounds by computational techniques

***Charles C. Peterson**[1], charliecpeterson@gmail.com, Deborah A. Penchoff[2], Howard L. Hall[3], Robert Harrison[4]. (1) Research Information Technology Services, University of North Texas, Denton, Texas, United States (2) , Institute for Nuclear Security, Knoxville, Tennessee, United States (3) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (4) Institute for Advanced Computational Science, Stony Brook University, Upton, New York, United States*

Simulating lanthanide and actinide chemistry with accurate computational methodologies is critical to better understand binding selectivity of heavy elements. This is crucial for designing separation agents, nuclear forensics, and understanding spectra. Accurate results from computational protocols need to include effects, such as relativity, spin-orbit coupling, and core correlation. Other effects, such as basis set choice and electrons needed in the correlation space are also needed for accurate representation of lanthanide and actinide compounds. Structural, thermochemical, and orbital population analysis as approaches to better understand the behavior of heavy element systems will be discussed.

NUCL 5

Electronic structure and chemical bonding of f-element coordination complexes with N,O,S-donor ligand

***Enrique R. Batista**, erb@lanl.gov, Jing Su, Ping Yang. Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Minor actinides found in spent nuclear fuel, such as Am and Cm, have isotopes with substantial radioactive half- lives that generate significant amounts of heat, which is detrimental to long-term waste storage. As a result, selective extraction of these actinides from spent reactor fuel is currently of great interest. The standard approach for selective separation of the species of interest is on the basis of liquid-liquid extraction processes where an extractant molecule preferentially binds to one of the ion. These extractant molecules typically have a non-polar tail that helps them migrate, through an organic-aqueous interface, carrying the ions and effectively separating them. Designing such extractants molecules is of high interest and it requires overcoming significant difficulties imposed by the similarity in chemical interactions between the lanthanides in solution and the late actinides, both of which tend to be in a +3 oxidation state. In this talk we will present a series of theoretical studies on the basis of electronic structure calculations to analyze potential extractant molecules based on N, O, S, and a combination of them. Our calculations aim at understanding the origin of the differences in their interactions with the intention to identify design principles and propose new ligands.

NUCL 6

Covalency of actinides (An^{III}, An^{IV}) with chelating agents across the actinide series

***Ping Yang**, pyang@lanl.gov, Morgan Kelley, Jing Su, Enrique R. Batista. Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Actinide-ligand bonding has a long history of investigation due to its importance to the nuclear fuel cycle, environmental remediation, nuclear medicine, and other concerns. Early actinides (up to plutonium) generally mimic some aspects of transition metal chemistry, including the formation of covalent An-ligand bonds through the 6d orbitals. Whereas the early actinides have seen extensive study, studies on the actinides heavier than plutonium are sparse. As the actinide series is traversed, the contraction of the 5f orbitals stabilizes the trivalent oxidation state, potentially limiting covalent interactions and enforcing lanthanide-like behavior. It is generally thought, therefore, that the heavier actinides do not form significant covalent interactions, though some evidence suggests this is not the case.

Our team recently investigated covalent interactions of both An(III) and An(IV) ions (An = Th to Es) across the actinide series as function of chelating agents using a few model systems.[1-5] The results clearly indicate the importance of the 5f orbitals in covalent actinide-ligand interactions across the actinide series. The changing nature of these

covalent interactions as the series is traversed provides new insights into the complexation of the actinides and will offer guiding principles for the design of new chelating ligands for this part of the periodic table.

NUCL 7

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by the ACS Division of Nuclear Chemistry and Technology). I wonder: A journey into the outer reaches of the periodic table

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

This lecture provides some glimpses into our trek across the actinide series that has now entered into its 20th year. We will detail the synthesis, structure elucidation, physical properties, and electronic structure of the heaviest elements for which this is possible. In particular, this talk will focus on how nonlinear changes in relativistic effects create discontinuities in periodicity that are particularly accute beyond curium (Z = 96). We will describe a number of unusual observations from the chemistry and physics of berkelium and californium.

NUCL 8

New uranyl chemistry mediated by redox-active ligands

*Ezra Coughlin[1], Yusen Qiao[3], Ekaterina Lapsheva[2], Matthias Zeller[1], Eric J. Schelter[2], **Suzanne C. Bart**[1], sbart@purdue.edu. (1) Department of Chemistry, Purdue University, West Lafayette, Indiana, United States (2) Dept of Chemistry, University of Pennslyvania, Philadelphia, Pennsylvania, United States (3) University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Uranyl derivatives are the most well-known actinide compounds, and they are characerized by their trans-dioxo arrangement. These U-O mulitple bonds are extremely strong, making such molecules persistant and difficult to transform. Our lab has demonstrated the use of redox-active ligands to activate strong uranium-element bonds in the past, and we have recently applied this methodology to break down uranyl containing species. We present the synthesis and characterization of new uranyl compounds featuring redox-active ligands, as well as analysis of their magnetic properties. Unusual paramagnetic, diradical uranyl species have been explored both for their electronic structure and uranyl functionalization chemistry. A rare example of scission of a U-O bond and conversion to an O-C bond is reported as well.

NUCL 9

Spectroscopic and binding constant studies of actinium chelation for targeted alpha therapy applications

***Benjamin W. Stein**[1], bstein@lanl.gov, Amanda Morgenstern[1], Maryline Kerlin[2,1], Laura Lilley[1], Stosh A. Kozimor[1], Enrique R. Batista[1], Ping Yang[1]. (1) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) University of Washington, Seattle, Washington, United States*

Actinium-225 (half-life, $t_{1/2}$=10 d) is a promising isotope for the treatment of metastatic cancers. During the decay of Ac-225 (and daughters), a total of 4 alpha particles are emitted, which gives Ac-225 uniquely high cytotoxicity. However, the use of Ac-225 has been hindered by both by an insufficient supply and a limited understanding of fundamental Ac chemistry. Los Alamos National Laboratories (LANL), is part of the Tri-Lab effort to develop an accelerator production capability using proton irradiation of natural thorium. In addition to addressing production, we have also been engaged in a cutting-edge research program focused on developing a wide variety of spectroscopic and physical techniques to interrogate the chemistry of Ac. Contrary to Ac-225, Ac-227 ($t_{1/2}$=22 y) is available in microgram amounts enabling the use of more traditional chemistry techniques. We have developed multiple spectroscopic and theoretical approaches to help understand Ac coordination chemistry, in particular X-ray absorption fine structure (XAFS) and nuclear magnetic resonance (NMR), supported by in-depth theoretical thermodynamic computations.

While Ac-227 has a much lower specific activity than Ac-225, the strong alpha/beta/gamma emissions of the daughter products have necessitated the development of careful handling protocols, both at LANL and at the Stanford Synchrotron Radiation Laboratory (SSRL). Additionally, the limited supply of Ac-227 necessitates full recovery of all material, ruling out any destructive measurement techniques. We will present our latest results on Ac coordination chemistry, involving the use of tetraazacrown ethers bearing phosphonate functional groups (DOTP). These spectroscopic results have demonstrated some subtle differences between actinium and its lanthanide homologue lanthanum. Thermodynamic calculations and binding constant measurements suggest that phosphonate-armed azacrown ethers may be a superior alternative to the commonly used acetate functional groups for trivalent actinide binding.

NUCL 10

Structural chemistry of tetravalent metal ion complexes and clusters: Assessing the impact of non-bonding interactions

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

Speciation underpins the chemical behavior of a metal ion. For the actinides, speciation depends largely on oxidation state, and our limited knowledge of the structural and energetic properties of tetravalent actinide complexes has posed significant challenges in our ability to predict An behavior under scenarios ranging from separations chemistry to environmental migration. To address this need, we have been examining the structural chemistry of tetravalent Ce, Th, U, and Pu complexes formed in the presence

of various counterions in an effort to understand the role that outer coordination sphere interactions have on the formation, stabilization, and precipitation of metal-chloride structural units. Recent results suggest that nonbonding interactions may play a key role in governing not only the isolation or crystallization of a dissolved unit, but also in determining the composition, charge, and stability of An(IV)-complexes and related metal-oxo clusters. Presented here will be an overview of recent efforts to elucidate the effects of outer- coordination sphere interactions on the structural chemistry of tetravalent metal ion (Ce, Th, U, and Pu) complexes. How the synthetic conditions, identity of the counter-ions, and nature of complexing ligands affect the speciation and reactivity of M(IV) building units as well as trends that can be discerned across the tetravalent actinides, Th-Pu, will be discussed.

NUCL 11

ARIES: From pits to plutonium oxide

***Jared T. Stritzinger**, jstritzinger@gmail.com, Daniel J. Garcia. AMPP-3, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

In 1996, the DOE office of Fissile Material Disposition began funding the prototyping of technology for the disposition of excess nuclear material at Los Alamos and Lawrence Livermore National Laboratories. At LANL, this took form in the Advanced Recovery and Integrated Extraction System (ARIES), which was dedicated in 1998 and has continued to operate since. With the United States and Russia signing the *Plutonium Management and Disposition Agreement (PMDA)* in 2000, both parties committed to each dispose of 34 metric tons of surplus weapon-grade plutonium. ARIES has provided the basis for the disassembly of pits and production of plutonium oxide. To date, the ARIES line has packaged 70 Lots (~1000 kg) of plutonium oxide for the Mixed Fuel Fabrication Facility. A review of the process line’s history from pit to packaged oxide, provides insight to the challenges of working with nuclear material and an opportunity to examine some of physical and thermal properties of plutonium oxide measured for each production lot.

NUCL 12

Targeted radionuclide therapy: The promise of short-lived alpha-emitting actinides

***Rebecca J. Abergel**[1,2], rjabergel@lbl.gov, dahlia An[2], Andrew Lakes[2], Gauthier Deblonde[2], Julian Rees[2], Stacey Gauny[2], Deepa Sridharan[2]. (1) Nuclear Engineering, University of California, Berkeley, Berkeley, California, United States (2) Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California, United States*

Targeted alpha-particle therapy holds tremendous potential as a cancer treatment, since it offers the potential of delivering a highly cytotoxic dose to targeted cells while minimizing damage to the surrounding healthy tissue, due to the short range and high linear energy transfer of alpha particles. While the only available FDA-approved radioimmunoconjugates utilize beta-emitting isotopes, I-131, Y-90, and Lu-177, a few actinide isotopes have recently emerged as promising short-lived radionuclides that emit multiple α particles in their decay chains, dramatically increasing the potential delivered dose. In particular, Ac-225 and Th-227 can act as in vivo alpha-generator radionuclides and are of great interest for new therapeutic applications.

To create a targeted alpha therapeutic, one must assemble 3 basic parts: a targeting moiety, a radionuclide binding molecule, and an appropriate radionuclide such as Ac-225 or Th-227. Though sound in theory, and despite promising therapeutic potential established in pre-clinical and clinical studies, such designs have been slow to emerge. Reasons for this protracted development are many, including limited radioisotope supply, insufficient understanding of isotope biodistribution and biodosimetry, poor retention of alpha-emitting daughter products at the target site, as well as inadequate chelation, one of the major drawbacks.

To seek further development of Ac-225 and Th-227 bioconjugate therapeutics, ongoing efforts aim at addressing all of those limitations. Our approach to clearly delineate the coordination chemistry and biodistribution of these radioisotopes, their short-lived daughter products, resulting dosimetry, mechanisms of induced cellular toxicity, efficacy, and safety will be presented and discussed.

NUCL 13

^{119m}Te production for ^{119}Sb radiopharmaceuticals

Stosh A. Kozimor[1]*, stosh@lanl.gov, Andrew Akin*[1]*, Kevin Bennett*[1]*, Eva Birnbaum*[1]*, Anastasia Blake*[1]*, Sharon Bone*[1]*, Mark Brugh*[1]*, Jonathan Engle*[2]*, Laura Lilley*[1]*, Michael Fassbender*[1]*, Veronika Mocko*[1]*, Francois Nortier*[1]*, Benjamin W. Stein*[3]*, Sara Thiemann*[1]*, Christiaan Vermeulen*[1]*. (1) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (2) University of Wisconsin, Madison, Wisconsin, United States (3) C-IIAC, Los Alamos National Laboratories, Los Alamos, New Mexico, United States*

Radionuclides find widespread use in in medical technologies for treating and diagnosing disease. Among the list of impactful radiotherapeutics,^{119}Sb stands out as having potential in targeted therapeutic applications of low energy electron emitting radionuclides. Developing ^{119}Sb based drugs has unfortunately been slow in comparison to other radionuclides, primarily because of limited access to this isotope. We contribute herein a production method that expands the available time for large-scale distribution and use. Our approach exploits production and isolation of longer-lived ^{119m}Te (4.7 d). This parent isotope slowly decays to ^{119}Sb, which in turn provides access to ^{119}Sb for a longer time period, in comparison to direct ^{119}Sb production routes. This presentation will describe target design, irradiation conditions, and the rapid radiochemical separation procedure for the ^{119m}Te/^{119}Sb pair. To guide process development and to understand why the separation was so successful, we also characterized the process using Te and Sb K-edge X-ray absorption spectroscopy (XAS). Ultimately the procedure provides a low volume aqueous solution that has

high ^{119m}Te (and consequently ^{119}Sb) specific activity in a chemically pure form. Currently, this procedure has been demonstrated at a large (production-size) scale and its product has high potential to meet stringent requirements of the FDA for a ^{119m}Te/^{119}Sb active pharmaceutical ingredient.

NUCL 14

Kinetics in f-element separations

***Mark P. Jensen**, mjensen@mines.edu, Gabriela A. Picayo, Madeleine A. Eddy. Colorado School of Mines, Golden, Colorado, United States*

Solvent extraction and associated techniques such as supported liquid membranes, extraction chromatography, and centrifugal partition chromatography are important approaches for isolating or separating particular lanthanides and actinides. Historically much of the work in developing these separations has focused on the thermodynamics of the metal-ligand interactions and tuning the ligand scaffold to produce optimal separations. However, solvent extraction is an inherently dynamic process, and the kinetics of the various chemical reactions and associated phase transport can be just as important as the thermodynamics in implementing real separations. Key features of the solvent extraction kinetics of actinide and lanthanide elements will be described and compared to the kinetics of other biphasic processes, for example heterogeneous catalysis. The role of advanced spectroscopic techniques in detecting and identifying intermediate species will also be considered. Although the complexity of solvent extraction systems with two distinct phases and the potential presence of multiple metal ions, counter ions, aqueous ligands, and organic extractants in a single extraction presents opportunities for counterintuitive effects on the kinetics, these effects can be indicative of the presence of specific intermediate species and particular rate determining steps.

NUCL 15

Lanthanide-based single-molecule magnets with high blocking temperatures

*Colin A. Gould[1], Philip C. Bunting[1], Selvan Demir[1,2,3], Randall R. McClain[4], Lucy E. Darago[1], Khetpakorn Chakarawet[1], Miguel Gonzalez[1,5], Katie R. Meihaus[1], Joseph Zadrozny[1,6], Michael Nippe[1,2,7], Jeffrey D. Rinehart[1,8], Simon J. Teat[2], Benjamin G. Harvey[4], William J. Evans[9], **Jeffrey R. Long**[1,2], jrlong@berkeley.edu. (1) University of California, Berkeley, Berkeley, California, United States (2) Lawrence Berkeley National Laboratory, Berkeley, California, United States (3) Michigan State University, East Lansing, Michigan, United States (4) Naval Air Warfare Center, China Lake, California, United States (5) Harvard University, Cambridge, Massachusetts, United States (6) Colorado State University, Fort Collins, Colorado, United States (7) Texas A&M University, College Station, Texas, United States (8) University of California, San Diego, La Jolla, California, United States (9) University of California, Irvine, Irvine, California, United States*

Scientists have long employed lanthanide elements in the design of materials with extraordinary magnetic properties, including the strongest magnets known, $SmCo_5$ and $Nd_2Fe_{14}B$. The properties of these materials are largely a product of fine-tuning the interaction between the lanthanide ion and the crystal lattice. Recently, synthetic chemists have begun to utilize f-elements—both lanthanides and actinides—for the construction of single-molecule magnets, resulting in a rapid expansion of the field. The desirable magnetic characteristics of the f-elements are contingent upon the interaction between the single-ion electron density and the crystal field environment in which it is placed. Taking advantage of this interaction, new approaches for synthesizing single-molecules magnets based upon lanthanide ions will be presented. Focus will be on recent work involving: (i) the use of an equatorial ligand field to create erbium(III) single-molecule magnets, (ii) high-temperature magnetic blocking and magneto-structural correlations in a series of dysprosium(III) metallocenium complexes, and (iii) the synthesis and characterization of radical-bridged dilanthanide complexes exhibiting strong magnetic exchange and high blocking temperatures. In addition, a means of achieving an electronic structure similar to lanthanide complexes with transition metals will be elaborated.

NUCL 16

Organometallic neptunium chemistry and the importance of spontaneous reduction reactions

Polly L. Arnold[1], *polly.arnold@ed.ac.uk, Tatsumi Ochiai*[1], *Jacob Shephard*[1], *Vikki Berryman*[2], *Michal Dutkiewicz*[1,3], *Olaf Walter*[3], *Roberto Caciuffo*[4], *Nikolas Kaltsoyannis*[5], *Simon Parsons*[1]. *(1) Univ of Edinburgh Sch of Chem, Edinburgh, London, United Kingdom (2) university of manchester, Manchester, United Kingdom (3) Directorate for Nuclear Safety and Security, Karlsruhe, Karlsruhe, Germany (4) Institute for Transuranium Elements, Karlsruhe, Germany (5) Department of Chemistry, University College London, London, United Kingdom*

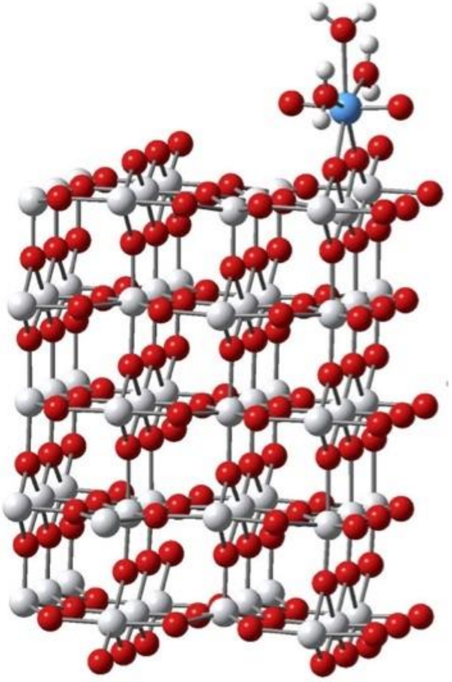
Studies of transuranic organometallic complexes provide particularly valuable insight into covalent contributions to the metal-ligand bonding, in which the subtle differences between the transuranium $An^{(III)}$ ions and their lighter lanthanide $Ln^{(III)}$counterparts are of fundamental importance for effective remediation of nuclear waste. Unlike the organometallic chemistry of uranium, which has focused strongly on $U^{(III)}$ with spectacular advances, that of the transuranics is significantly technically more challenging and has remained dormant. We will show recent and new, electron-rich neptunium organometallic compounds and discuss how the differences in redox stability between the early actinide metal cations is readily modified by apparently subtle changes in the organometallic ligand set.

NUCL 17

Actinides on surfaces

***Georg Schreckenbach**, schrecke@cc.umanitoba.ca. Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada*

The interaction of actinide species with surfaces is relevant for a number of different reasons, including environmental transport, reduction at surfaces or filters. Modelling such interactions adds a level of complexity to the more conventional molecular calculations. We will present our work on two different types of surfaces that can interact with actinide species such as uranyl, UO_2^{2+}, TiO_2 surfaces that have been observed in geological systems to be associated with uranium reduction from U(VI) to U(IV) and 2-dimensional materials.



NUCL 18

Exploiting crystal structure–property relationships to characterize uranium materials

***Ashley Shields**[1], ashley.shields@gmail.com, Andrew Miskowiec[2], Marie C. Kirkegaard[1], Jennifer Niedziela[1], Roger Kapsimalis[1], Brian Anderson[1]. (1) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Characterizing new materials or unknown polycrystalline solids is a long-standing challenge for chemists. By analyzing basic crystalline building units, we hope to reduce the characterization problem of low-symmetry systems down to fundamental units. We

present an analysis of coordination geometries of over 3,500 uranium oxide and uranium fluoride structures. These structures have been generated using a combination of the structure prediction package Universal Structure Predictor: Evolutionary Xtallography(USPEX), which uses genetic algorithms to search for stable phases, and density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP) to evaluate the energetics of each predicted structure. This generates a database of structures and energies that is biased toward experimentally favorable compositions (e.g., UO_2, UO_3) but still searches previously unreported compositions.

We have employed the Coordination Environments module in pymatgen to analyze the coordination geometries of all cation sites (i.e., uranium sites) in the database and correlate these geometries with the DFT energies calculated by VASP. The database contains 56 of the 65 IUPAC–approved crystal polyhedra, with cubic, octahedral, and square-face capped trigonal prism being the most common coordination geometries. We present our progress toward correlating vibrational properties, such as phonon modes, with the fundamental coordination environments, with the aim of facilitating interpretation of experimental analytical data including infrared, Raman, and neutron scattering spectroscopies to characterize complex uranium oxide phases.

NUCL 19

Understanding the polymorphism of $A_4[(UO_2)_3(PO_4)_2O_4]$ (A=alkali metals) uranyl phosphate framework structures using density functional theory

Vancho Kocevski, *kocevski@mailbox.sc.edu, Theodore Besmann. Nuclear Engineering Program, University of South Carolina, Columbia, South Carolina, United States*

In this study we used density functional theory (DFT), in the form of DFT+U method, calculations to gain an insight into the polymorphism of $A_4[(UO_2)_3(PO_4)_2O_4]$ (A = Na, K, Rb, Cs) uranyl phosphate structures, specifically the difference between 3D uranyl phosphate and a family of recently described layered uranyl phosphates. Variation of the computed properties with changes in U_{eff}-values are also studied. The DFT results agree with the experimental observations, showing that the Cs-containing 3D polymorph and the K-containing layered polymorphs are more stable than their respective layered and 3D polymorph. We show an increase in the difference between the total energies of the layered and 3D polymorphs, and an increase in the band gaps with increasing U_{eff}-value. For each of the studied polymorphs we calculated the electronic, optical and bonding properties. We also show an anisotropy in the absorption indexes along the three crystallographic directions of the polymorphs, which is especially noticeable in the layered polymorphs. We attribute the difference in the density of states on the different coordination of the U atoms in the layered and 3D polymorphs. We attribute the preferred formation of the 3D Cs polymorph to the substantial increase in the U–A bond strength, which is more pronounced than the differences in the bond strength between structures for the other atomic pairs.

NUCL 20

Evaluation of van der Waals interactions in uranium phases using density-functional theory (DFT) using the exchange-hole dipole moment (XDM) dispersion correction

Matthew Christian[1]*, mchristian@dal.ca, Erin R. Johnson*[2]*, Theodore Besmann*[1]*. (1) University of South Carolina, Columbia, South Carolina, United States (2) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada*

Density-functional theory (DFT) is a powerful tool to investigate properties of nuclear materials. However, there are unique challenges to modeling nuclear materials due to the complex electronic structure of actinide and lanthanide elements. Conventional DFT functionals lack the long-range, non-local correlation needed to calculate dispersion interactions, but they can be accounted for by adding a correction to the DFT energy. However, many DFT studies of nuclear materials neglect the inclusion of van der Waals interactions because they are assumed to marginally affect both structure and energies. In this work, we present a study of several uranium containing compounds (e.g., U, UCl3, UF3, UO2, USi3, U3Si) using DFT, incorporating the exchange-hole dipole moment (XDM) dispersion model. Our results will show how incorporating a dispersion correction affects crystal structure and Hubbard U parameter. The results will be compared to experimental values where available.

NUCL 21

Role of extractant structure in the self-association and phase behavior of uranyl nitrate complexes in organic solvents

Michael Servis[1]*, michaelservis@gmail.com, David Wu*[2]*, Jenifer Shafer*[3]*, Aurora E. Clark*[4]*. (1) Washington State University, Pullman, Washington, United States (2) Dept. of Chemistry Geochemistry, Colorado School of Mines, Golden, Colorado, United States (3) Colorado School of Mines, Golden, Colorado, United States (4) Washington State Univ, Pullman, Washington, United States*

The distribution and phase behavior of uranyl nitrate, extracted from acidic aqueous solutions by solvating organophosphorus extractants into nonpolar organic solvents, depend on their association in solution.[1,2] That association is investigated with molecular dynamics simulations and density functional theory calculations.[3] Uranyl nitrate complexes are found to form long-range isotropic pairs and short-range ordered dimeric assemblies. The short-range pairs feature a unique square configuration comprised of noncovalent interactions mediated by the ligand and acid anion. The stability long-range pair depends on extractant alkyl tail chain length while the short-range assembly is affected by changes to the structure of the extractant's polar head group. The stability of these species is further affected by the solvation environment and molecular structure of the organic solvent. At sufficiently high uranyl nitrate concentration, it is known experimentally that the organic phase partitions into two

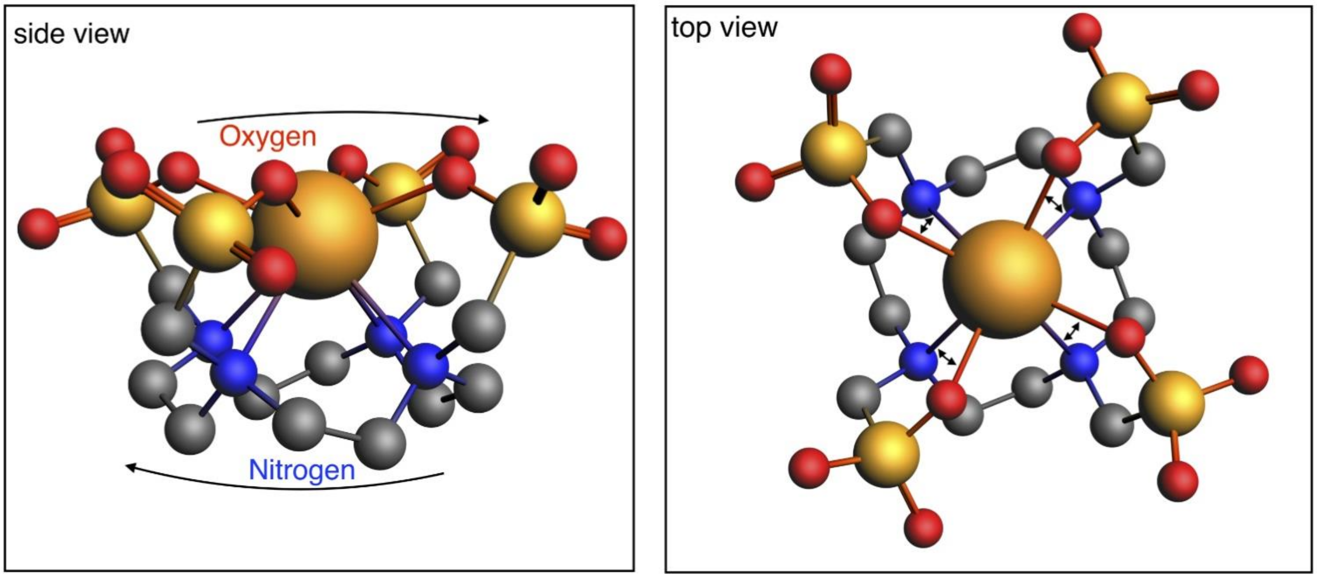
phases, one of which contains most of the extracted polar solutes.[1,2] Simulations of such conditions show the short- and long-range pairs described above form extended clusters, revealing the mechanism of the phase transition. The role of extractant and solvent structure on the phase behavior of the high loading organic phase can therefore be connected to their impact on the pairwise association of the uranyl nitrate complexes.

NUCL 22

Computational design of actinium-225 chelators for use in targeted alpha therapy

Amanda Morgenstern, *amorgenstern@lanl.gov, Laura Lilley, Benjamin W. Stein, Stosh A. Kozimor, Enrique R. Batista, Ping Yang. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Actinium-225 is an excellent candidate for targeted radiotherapy to treat cancer and infections due to its half-life of ten days and emission of four high-energy alpha particles. In order to harness and direct the energetic potential of actinium, strongly binding chelators must be developed that are capable of retaining actinium ions until they reach the biochemical target. Little work has been done to understand the bonding properties of actinium, making the development of chelating ligands a challenging task. In this talk I will present a systematic theoretical study, done in collaboration with experimentalists, to elucidate the unique bonding properties of macrocyclic chelating agents varying in ring size, coordination number, and functional groups. We first identify the optimal ring size and coordination number of the chelates for actinium binding based on thermodynamic analysis. Using this information, we explore attaching different functional groups to various positions on the rings. We then perform a structure and bonding analysis of proposed chelators to determine which features of chelating molecules are desirable for optimal actinium binding. The fundamental bonding information that is gained for actinium through this study can be used as a driving force in the design process for multifunctional chelators.



The small twist angle between the ring nitrogen atoms and the phosphonate oxygen atoms in DOTP enhances actinium binding.

NUCL 23

Bonding in the actinide series: Using EXAFS to systematically probe coordination compound structures of Th through Cf

Corwin Booth*, chbooth@lbl.gov, Gauthier Deblonde, Liane M. Moreau, Julian Rees, Rebecca J. Abergel. Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States*

Recent work on the chemistry of the actinides has seen a larger focus on actinides outside of Th, U, Np, and Pu. In particular, the number of studies featuring Bk has allowed for a more thorough look at the entire actinide series up to Cf. Here, the local structure of actinide coordination compounds of Th through Cf using the EXAFS technique are presented in order to begin to elucidate the fundamental bonding interactions, presenting a fresh look at understanding the roles of covalence and structure. The EXAFS technique allows for a broad look at many complexes due to its ability to obtain structural information on microgram quantities of material in the liquid form. Ligands are typically chosen in relation to separations and chelation strategies, including bio-inspired hydroxypyridinone hard oxygen-donors and about a dozen other ligands. The structural results are presented in the context of other characterizations, including luminescence, and in their relation to protein interactions. Combined with theoretical predictions, these data add significant insight to the field of actinide chemistry, and may lead to innovative characterization methods and separation processes.

NUCL 24

Plutonium physics and chemistry highlights from Los Alamos National Laboratory: Neutron and NMR spectroscopy

***Eric D. Bauer**, edbauer@lanl.gov. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Pu is arguably the most complex elemental metal in the periodic table because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. Metallic δ-Pu exhibits a Pauli-like magnetic susceptibility, electrical resistivity, and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. In this talk, I highlight our inelastic neutron and nuclear magnetic resonance (NMR) spectroscopy used to understand the physics and chemistry of plutonium and Pu compounds. Prof. Albrecht-Schmitt played a critical role in several of our studies of Pu compounds over the years and has been a cheerleader for many others.

We investigated the magnetic fluctuation spectrum of δ-Pu via inelastic neutron scattering using the ARCS spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory [1]. Our study reveals that the ground state of plutonium is governed by valence fluctuations, that is, a quantum-mechanical admixture of distinct 5f electronic configurations. Our results, which are in quantitative agreement with dynamical mean field theory calculations, show that the magnetism in Pu is not "missing" but is dynamic and driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of δ-Pu.

Nuclear magnetic resonance spectroscopy has developed into a cornerstone of chemistry and medicine for determination of the structure of chemical and biological systems through spin-1/2 ^{1}H and ^{13}C NMR, and for imaging the body. The spin-1/2, ^{239}Pu NMR signal was only recently observed in cubic PuO_2, despite more than 50 years of effort on a range of ^{239}Pu compounds [2]. We report the second observation of a Pu-239 NMR signal in a tetragonal compound PuB_4. This compound is predicted to be a topological insulator [3] and measurements of the NMR shift reveal a significant difference (~25%) in the shift between PuO_2 and PuB_4, suggesting large changes in bonding in the two materials. Our 2nd observation of the Pu-239 NMR signal in PuB_4 opens up a new window into understanding chemical bonding, aging, and correlated electron phenomena in Pu and its compounds [4].

NUCL 25

How f-block atoms behave in intermetalloid clusters: [Ln@Zintl] and [Ac@Zintl]

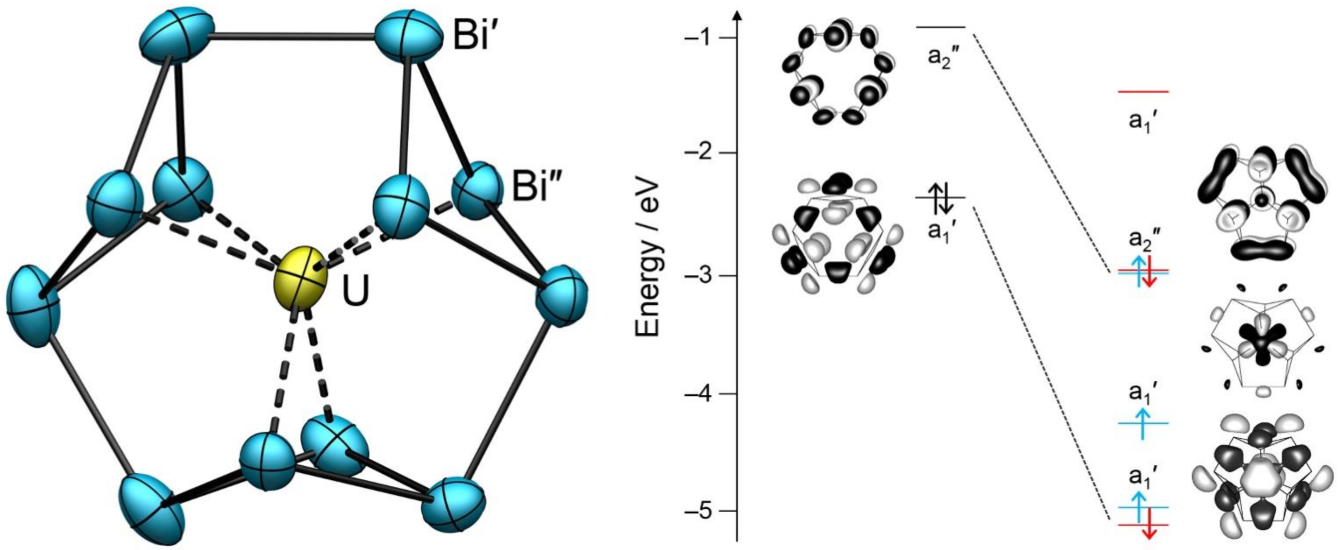
***Stefanie Dehnen**, dehnen@chemie.uni-marburg.de. Chemistry, Philipps-Universität, Marburg, Germany*

Intermetalloid clusters, consisting of a main group (semi-)metal shell that embeds one or more transition metal atoms(s), have been actively investigated by many research groups over the past decades, regarding basic properties as well as their potential use as innovative materials.

Some years ago, pnictogentrielide or pinctogentetrelide ions $[E^{13/14}{}_{x}E^{15}y]^{q-}$ ($E^{13/14}$ = Ga, In, Tl; Ge, Sn, Pb; E^{15} = As, Sb, Bi) proved to be useful synthetic tools for the access of ternary intermetalloid clusters $[M_{x}@E^{13/14}{}_{y}E^{15}{}_{z}]^{q-}$ by reactions with transition metal (M) compounds. These experiments also allowed first access to corresponding clusters with interstitial lanthanide cations.

Recently, we extended our studies towards comprehensive exploration of the formation pathways, towards clusters with very unusual geometric and electronic structures, and towards intermetalloid clusters embedding actinide ions.

While most of the clusters may be understood in terms of (semi-)metal cages that are doped by the interstitial transition metal or lanthanide ions, actinide ions have an even greater impact on the structure and bonding within such species, owing to the involvement of f electrons.



Molecular structure and frontier orbital scheme of the intermetalloid cluster $[U@Bi_{12}]^{3-}$

NUCL 26

Californiums moving to Colorado

*Nathan Bessen[1], Morgan Kelley[2], Jing Su[2], Enrique R. Batista[2], Ping Yang[2], **Jenifer Shafer**[1], jshafer@mines.edu. (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*

While Thomas’ career has spanned many aspects of actinide coordination chemistry, arguably the most transformative, and certainly the most relevant for my career, was the discovery of covalency in the bonding of heavy actinide (i.e. transcurium) coordination complexes. This information was disseminated to me the first time at the 2013 ACS Meeting in New Orleans and had an indelible, extremely positive impact regarding the development of the radiochemistry program at the Colorado School of Mines. This presentation will highlight how the discovery of transcurium covalency encouraged further development of the radiochemistry program at Mines and, ultimately, californium-249 moving to Colorado. Current efforts examining transcurium solution coordination chemistry and thermodynamics will also be presented with a significant emphasis on recent findings relevant to thiodiacetate and thiophenediacetate complexes

NUCL 27

Soft X-ray synchrotron radiation studies of actinide materials

***David K. Shuh**, DKShuh@lbl.gov. Lawrence Berkeley National Laboratory, Berkeley, California, United States*

The soft X-ray synchrotron radiation methodologies near-edge X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) have been developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL) to elucidate the electronic structure of radioactive materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of actinide materials, complexes, ligands, and the overall understanding of actinide materials. The experimental developments at the ALS have largely centered on studies of radioactive materials with the Molecular Environmental Science (MES) soft X-ray scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for spatially-resolved investigations. The spectromicroscopy capabilities of the STXM provide the means to determine the speciation and composition in a range of actinide materials, particularly those of technological and environmental interest with spatial resolution that can reach to the true nanoscale. A particular emphasis has been on the use of the light atom (B, C, N, O, F, Na, Mg, Al, Si) ligand K–edge XAS technique to determine the electronic structure characteristics in an array of unique and relevant radioactive materials. Furthermore, there are a host of additional electron energy level thresholds (such as the L–edges of the transition metals, the M–edges of the lanthanides that and cesium plus others) that can be probed by near-edge XAS in the soft X-ray region. Recently, STXM spectromicroscopy studies have been extended to fast ion beam (FIB) prepared radioactive and irradiated material specimens in collaboration with Idaho National Laboratory. Complementing STXM spectromicroscopy are results from soft x-ray XAS/XES investigations that have largely centered on the actinide dioxides. The XES/XAS studies have investigated the nature of the electronic structure by probing both low-lying actinide and oxygen edges.

NUCL 28

Protactinium and the intersection of actinide and transition metal chemistries

***Richard Wilson**, rewilson@anl.gov. Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States*

The periodic stabilization of the 5f orbitals across the actinide series gives rise to the fascinating chemical behavior that is the hallmark of these elements' chemistry. Often overlooked is the chemistry of protactinium, Z = 91. Our hypothesis has been that protactinium sits at a chemical intersection of transition metal and actinide chemistries. Experimentally, we studied whether or not protactinium forms a hexametalate like those for niobium and tantalum. Computational studies investigated the stability and the electronic properties of our synthesized protactinium complexes, along with those of Nb, Ta, and U focusing on the periodic chemical differences between them. Presented here are our studies of the changing chemistries between the transition metals and the actinides, highlighting their intersection at protactinium and the position of the actinide elements within the broader periodic system.

NUCL 29

Selective separation of Zr(IV) from Pu(IV) for used nuclear fuel reprocessing applications

***Nathalie A. Wall**, nawall@wsu.edu, Mitchell Friend. Chemistry, Washington State University, Pullman, Washington, United States*

Uranium-235 and plutonium-239 fission to produce zirconium – including stable, long-lived, and short-lived Zr isotopes –, with Zr concentrations similar to those of Pu for several reactor designs. The co-extraction of Zr(IV) with U(IV) and Pu(IV) during the reprocessing of used nuclear fuel presents a challenge for the nuclear industry and a selective separation of Zr from Pu(IV) is needed. A ligand-driven Pu precipitation presents a concern from a proliferation standpoint, but polyaminopolycarboxylate ligands are promising contenders as Zr holdback reagents. Our work on the determination of thermodynamic data for complexes of Hf(IV) (Zr analog), Zr(IV), and Pu(IV) with oxalate and various polyaminopolycarboxylate ligands indicates that *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CDTA) is a favorable candidate. We determined the 1:0:1 CDTA complex stability constants for Zr(IV) and Pu(IV) to be 29.6 and 24.2 (log units), respectively Additionally, a new 1:4:2 Zr complex was identified with a stability constant of 58.5 (log units) and the 1:2:1 Pu complex stability constant is 25.8 (log units). Calculations based on our thermodynamic data show efficient Pu(IV)/Zr(IV) separations with 0.1 M CDTA, with a Pu/Zr separation factor varying between 125 and 7, in a solvent extraction systems using 0.1 M of the extractant thenoyltrifluoroacetone (TTA) and with an aqueous phase with a 0.1 - 1.0 M acid concentration range.

NUCL 30

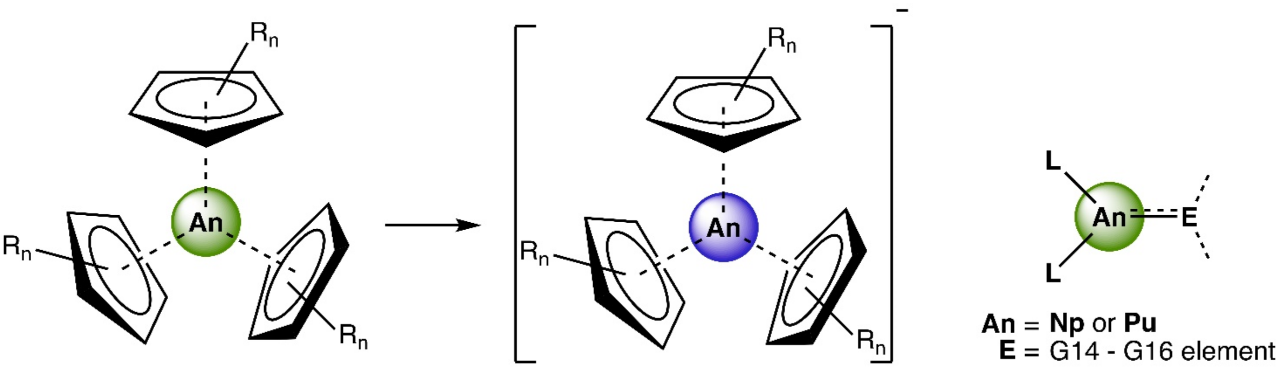
Trans-uranic organometallic chemistry: Oxidation states, bonding, and electronic structure

Conrad A. Goodwin[1], *cgoodwin@lanl.gov, Niels Lichtenberger*[3], *Stosh A. Kozimor*[1], *William J. Evans*[2], *Andrew Gaunt*[1]. *(1) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Dept of Chemistry, University of California Irvine, Irvine, California, United States (3) Philipps-Universität Marburg, Marburg, Germany*

The actinides (An) occupy an intriguing place in the periodic table, where 5f-orbitals are potentially available to engage in bonding, in contrast to the more core-like properties of the lanthanide (Ln) 4f orbitals. the energy levels and radial extent of the 5f orbitals can compete with 6d-orbitals in bonding regimes. These effects are such that An–E (E = G13–G17) bonds often occupy a distinct region between being (essentially) ionic such as Ln–E bonds, or highly covalent like TM–E (TM = d-block elements such as iron) bonds.

Studies into the electronic and bonding properties of Th and U have blossomed over the past 15 years, in no small part due to facile access to a diverse range of anhydrous precursors which have allowed fascinating new An–E bonds and even new oxidation states to be investigated by multidisciplinary techniques. The transuranic actinide elements (Np–Lr) have suffered in these regards due to a paucity of starting materials, which when coupled with inherent difficulties in obtaining and handling these highly radioactive materials in specialist facilities has slowed progress into detailed electronic and bonding investigations of these elements. Nevertheless, coordination complexes of elements up to Cf have been reported.

Recent advances in the availability of anhydrous Np and Pu precursors has allowed an entry into the study of examples of organometallic complexes with these elements for the first time, along with reports of formal An(II) complexes with these elements for the first time as molecular species. Recent results pertaining to Np, Pu, and Am organometallic chemistry that facilitate the pursuit of complexes containing formal An^{2+} ions will be discussed (**1**), along with efforts to isolate metal-ligand multiple bonds and new molecular bonding motifs containing a significant degree covalent bonding interactions (**2**).



An = Np–Am **1** **2**

NUCL 31

Analytical chemistry in support of plutonium production

Justin N. Cross, *justin.n.cross@gmail.com, Angela C. Olson, Lav Tandon. Chemistry Division, Los Alamos National Lab, Los Alamos, New Mexico, United States*

As part of Los Alamos National Laboratory’s support of national security missions, LANL maintains the capability to prepare, cast, and fabricate plutonium metal . The Actinide Analytical Chemistry group supports these capabilities with robust chemical characterization, certifying that a material is suitable for its intended use. This talk will focus on the analytical chemistry sustaining this certification. The techniques discussed will include Pu assay, Fe assay, Ga assay, anion analysis, plasma spectroscopy, and Mass spectrometry. Challenges associated with making these measurements on Pu and achieving high accuracy, precision and low uncertainty will also be discussed.

NUCL 32

Actinide chemistry at the most fundamental and comprehensible level: Gas-phase reactions

John K. Gibson, *jkgibson@lbl.gov. Lawrence Berkeley National Laboratory, Emeryville, California, United States*

The contemporary focus of actinide chemistry is on solids and solutions, which is in alignment with the broader field of inorganic chemistry and particularly the subset of transition metals. Gas-phase studies of simple isolated species, absent condensed phase perturbations and resultant complexities, can provide foundational understanding and have thus long been a primary purview of physical chemistry. An enduring goal of gas-phase actinide chemistry is to bridge the artificial schism between inorganic and physical chemistry, employing very elementary systems to provide fundamental insights that may be elusive amid the complexities of condensed phases. Ongoing endeavors in gas-phase actinide chemistry focus on unimolecular and bimolecular reactions in which

essential reactivity can be revealed and tuned, and whereby new oxidation states can be discovered. A key attribute of these efforts is inclusion of at least a few actinides, and often several, to identify potentially enlightening trends across the series. Representative recent results from this venture will be presented.

NUCL 33

Recent advances in actinide ligand multiple bonding

Stephen T. Liddle[1]*, steve.liddle@manchester.ac.uk, Jingzhen Du*[1]*, Lucile Chatelain*[1]*, Michal Dutkiewicz*[1]*, Olaf Walter*[2]*. (1) School of Chemistry, The University of Manchester, Manchester, United Kingdom (2) ITU Karlsruhe, Karlsruhe, Germany*

There is currently great interest in the nature and reactivity of molecular actinide-ligand multiple bonds. This is because the nature and extent of 5f/6d orbital participation in actinide-ligand bonding is still a topic of debate, and the unique orbital-hybridisation patterns available to across the series promises novel reactivity and magnetism. We have found that certain triamidoamine ligands are exceptionally effective at stabilising unprecedented actinide-ligand multiple bonds involving main group fragments of interest in their own right. This talk will provide an update on our recent progress regarding nitrides and if time allows we will describe our recent forays into transuranic research.

NUCL 34

Differentiating f-elements from ion-specific electronics and coordination environments

Eric J. Schelter*, schelter@sas.upenn.edu, Thibault Cheisson, Bren E. Cole, Yusen Qiao, Joshua Nelson, Robert Higgins. Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Efficient f-element separations remain a perennial challenge. We have been interested in triggering element-specific changes, for example through electronic structure differences, to achieve efficient separations through new thermodynamic modes. And in an orthogonal approach, to express differences in metal complexes through variable rates of some chemical change – a separations chemistry through kinetics. Both methods allow direct connection of coordination chemistry to macroscopic properties for separations. These connections have enabled new modes in solid-liquid extraction in an effort to complement solvent extraction for specialized applications. For this talk, our latest results on chelating and redox active ligand frameworks and their applications in thermodynamic and kinetic separations of elements will be presented.

NUCL 35

Oak Ridge National Laboratory’s Isotope Program: Unique and dynamic

***Julie Ezold**, ezoldjg1@ornl.gov, Susan Hogle. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Oak Ridge National Laboratory (ORNL) has a long history in the production of isotopes, heavy elements, and more recently in the discovery of super heavy elements (SHEs). Even though ORNL originated as part of the Manhattan Project, developing processes and techniques for the production, separation, and purification of 239 Pu in 1944, its name has become synonymous with a wide range of isotopes. Two of ORNL's unique facilities— Radiochemical Engineering Development Center and High Flux Isotope Reactor Research, are instrumental in the research and development of novel production techniques as well as chemical separations. Research into innovative methods for the transmutation of curium to heavier actinides and development of thin actinide targets for SHE discovery is at the forefront of ORNL's Isotope Program.

NUCL 36

From actinides to superheavies and to the stars

***Christoph Duellmann**, duellmann@uni-mainz.de. Institute of Nuclear Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany*

Much is known about the lighter actinides. Information becomes more scarce beyond Am and Cm, yet the properties of the heavy actinides, near and dear to Tom's heart, are no less intriguing. Availability becomes a core issue beyond Fm, where the boundary to atom-at-a-time studies is crossed. My interaction with Tom Albrecht-Schmitt was triggered by his expertise in actinide chemistry paired with the desire to go the full length to the end of the actinide series, where methods of synthesis of single-atom elements are required, as they are routinely applied in our studies of superheavy elements. I will briefly describe some the recently used methods in the study of heavy actinides, then highlight chemical studies of superheavies, and finally reach for the stars from where we have recently learned how nature produces actinides in astrophysical events.

NUCL 37

From trivalent actinide borate complexes to cationic materials

***Matthew Polinski**, polinskimj@gmail.com. Chemistry, Bloomsburg University of Pennsylvania, Bloomsburg, Pennsylvania, United States*

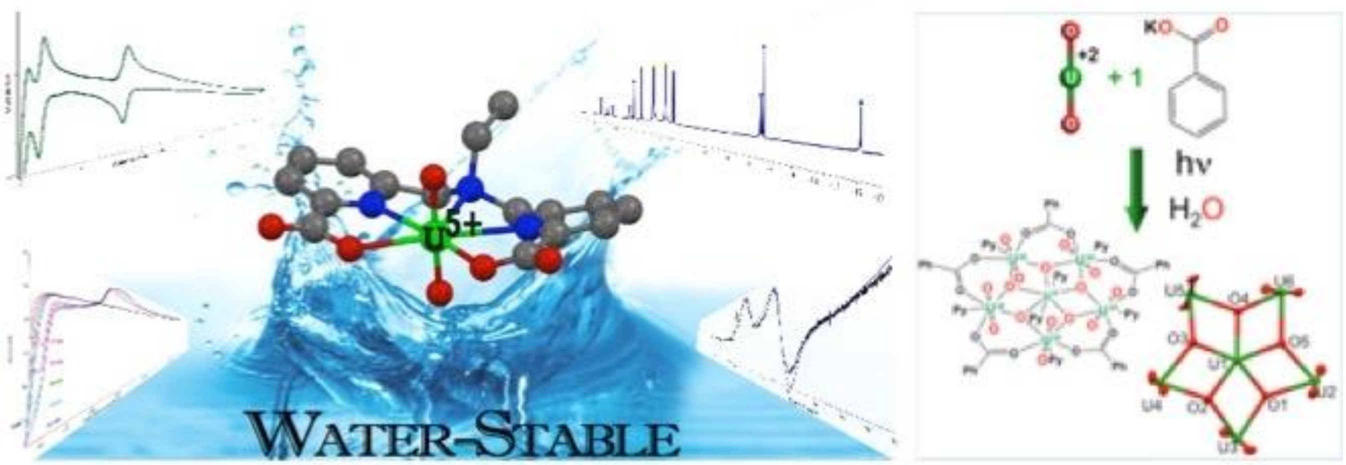
Exploring the fundamental chemistry present in the late actinides has yielded many fascinating and unexpected discoveries. From the unforeseen involvement of the *f*-orbitals in the chemical bonds of some trivalent actinide borate materials to californium acting as a second chemical transition point in the 5*f*-series, the research conducted in the Albrecht-Schmitt lab has been at the forefront of the recent knowledge boom in *f*-element chemistry. This talk will present the chemistry of the trivalent *f*-element borate compounds with a focus on chemical bonding and the unusual behavior of Californium. Additionally, how this previous work has influenced the current research conducted in the author’s lab with undergraduate students – exploration of cationic materials for nuclear waste remediation and synthetic routes to stabilize divalent Europium complexes – will be discussed.

NUCL 38

Recent developments in uranium(V) chemistry

Marinella Mazzanti, *marinella.mazzanti@epfl.ch. Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*

The chemistry of uranium(V) compounds remains less developed compared to U(IV) and U(VI) ones in spite of the relevance of U(V) species in environmental remediation, materials science and catalysis. Here we will report different routes leading to stable U(V) and uranyl(V) containing species both in organic and water solution and we will discuss the various parameters determining the stability of these species. In particular we will show that suitable polydentate ligands can lead to water stable uranyl(V) complexes. We will also present the incorporation of U(V) in cluster compounds during the photochemical reduction of uranyl(VI) or the uranyl(V) disproportionation. Moreover, we will report the interesting magnetic and reactivity properties of some of U(V) compounds including their implication in dinitrogen reduction.



NUCL 39

Efficient removal of radionuclides from aqueous solutions using carbon nanomaterials

***Xiangke Wang**, xkwang@ncepu.edu.cn. North China Electric Power University, Beijing, China*

This page presents the surface modification of carbon nanomaterials (carbon nanotubes, graphene oxides) using different functional groups and their application for the efficient and selective elimination of radionuclides from aqueous solutions. The interaction mechanism between radionuclides and carbon nanomaterials was studied by batch sorption experiments, surface complexation modeling, spectroscopy analysis (XPS and EXAFS) and theoretical calculations. The results showed that the carbon nanomaterials have high sorption capacity in the preconcentration of radionuclides from large volume of aqueous solutions, and the surface grafting functional groups could enhance the selectivity of radionulcides from solutions. The interaction of Eu(III), Am(III) and U(VI) with graphene oxides and carbon nanotubes were studied under different experimental conditions, and the difference in the interaction of trivalent lanthanides and actinides were found quite different under same experimental conditions, which were quite different from the physicochemical behaviors of lanthanides and actinides on clay minerals and oxides. The difference was attributed to the surface properties of nanomaterials and the radionuclides.

The following Figures show the interaction of Eu(III) and Am(III)-243 with carbon nanotubes and the interaction of U(VI) with graphene oxides with different functional groups. From the DFT calculations, the bind energy of radionuclides with different functional groups are quite different. More detailed results and discussion are present in the references.

NUCL 40

Actinide polyrotaxane compounds: From structural diversity to inclusion effect

***Weiqun Shi**, shiwq@ihep.ac.cn, Lei Mei, Zhifang Chai. Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, Beijing, China*

Actinide polyrotaxane compounds, which represent a type of topologically unique actinide compounds, definitely show different assembly modes of actinide ions with supramolecular systems compared to other transition metal and lanthanide metal ions. Our group conducted the related studies of actinide-organic rotaxane compounds and we have succeeded in the preparation the first case of uranyl-organic rotaxane compounds with a unique ‘dragon-like’ twist under hydrothermal conditions, which is induced by the specific coordination pattern of uranium and stabilized by hydrogen bonding between the η^1-mode carboxylate group and adjacent methylene moieties of CB[6]. As the unprecedented extension of actinide-rotaxane complexes from uranium to transuranium, we also reported the first crystal structure of neptunium-rotaxane complex, of which the intriguing interwoven neptunium(V)-rotaxane coordination network incorprating mechanically-interlocked [*c*2]daisy chain unit is promoted by simultaneous coordination of cucurbituril (CB6) and carboxyl groups from axle molecules in pseudorotaxane to Np^V. The exploration of this new type of structurally unique actinide-bearing supramolecular architectures has a stimulative effect on the pursuit of other special ligands for actinides and new types of actinide entangled structures with more complex assembly modes. Simple non-extended transuranium polyrotaxane compounds formed by volatilization or diffusion method are also expected in the future.

NUCL 41

Efficient separation and remediation of $^{99}TcO_4^-$ under extreme conditions using advanced cationic porous materials

***Shuao Wang**, 30085961@acs.org. Soochow University, Suzhou, Jiangsu, China*

Direct removal of $^{99}TcO_4^-$ from the highly acidic solution of used nuclear fuel at the first stage when the used fuel rods are dissolved would be highly beneficial for the subsequent solvent extraction of uranium and plutonium and more importantly aids in the elimination of ^{99}Tc discharge into the environment during the vitrification process and waste management. However, this task represents a huge challenge given the combined extreme conditions of super acidity, high ionic strength, and strong ionizing radiation field. A qualified anion-exchange material aimed at this goal would require high stability in acids, decent radiation-resistance, high TcO_4^- uptake kinetics and capacity, and excellent sorption selectivity and this type of material has yet to be reported. Here we substantially overcome this challenge using a non-crystalline cationic polymeric network, SCU-CPN-1. It possesses unprecedented TcO_4^- uptake capabilities in at least four different aspects: the fastest sorption kinetics, the highest sorption capacity, the most promising uptake performance from highly acidic solutions, and excellent radiation-resistance and hydrolytic stability among all anion sorbent materials reported to date. This leads to efficient TcO_4^- separation from two different types of simulated nuclear waste solutions: used fuel reprocessing solution in 3 M nitric acid and Hanford Low Activity Waste (LAW) Melter Recycle Stream. In addition, this material is fully recyclable for multiple sorption/desorption trials based on the observed complete anion-exchange process, making it extremely attractive for waste partitioning and even emergency remediation tasks. The excellent TcO_4^- uptake capability was further elucidated by synchrotron radiation X-ray absorption spectroscopy, solid-state NMR measurement, and density functional theory analysis on anion coordination and bonding.

NUCL 42

Recent advances in low oxidation state actinide chemistry

***William J. Evans**, wevans@uci.edu. Dept of Chemistry, University of California Irvine, Irvine, California, United States*

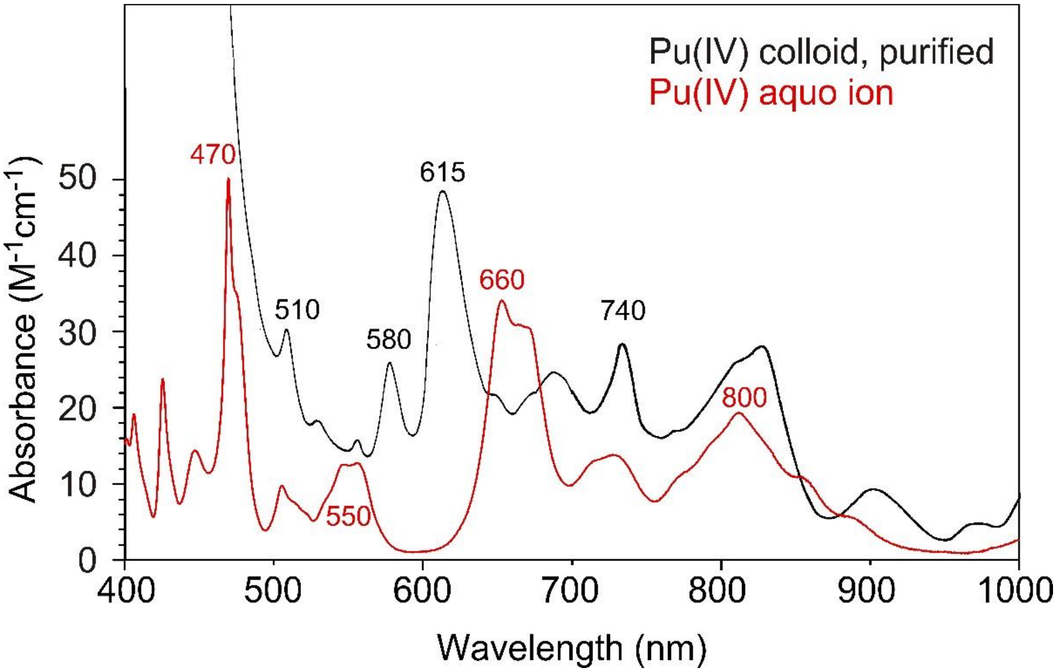
Recent results in the chemistry of the actinides in oxidation states less than +4 will be described and compared with the latest advances in low oxidation state rare-earth metal chemistry. It is now known that the +2 oxidation state is accessible in crystallographically-characterizable molecular complexes of Th, U, Np, and Pu. Th(II) was found in $(Cp''_3Th)^{1-}$ and U(II) in $(Cp'_3U)^{1-}$ and $(Cp''_3U)^{1-}$ where Cp' = $C_5H_4SiMe_3$ and Cp'' = $C_5H_3(SiMe_3)_2$. Np(II) and Pu(II) were isolated in $(Cp''_3An)^{1-}$ complexes synthesized at Los Alamos National Laboratory in collaboration with A. J. Gaunt, S. A. Kozimor, and co-workers. Isolation of these four An(II) species allows a comparison with Ln(II) complexes which have been found to exist in three categories: traditional Ln(II) ions with $4f^{n+1}$ electron configurations, (Eu, Yb, Sm, Tm), new Ln(II) ions with $4f^n5d^1$configurations (La, Ce, Pr, Gd, Tb, Ho, Er, and Lu), and configurational crossover Ln(II) ions that can have either configuration depending on the ligands (Dy and Nd). The new actinide complexes will be compared with the rare-earth compounds in terms of synthesis and the dependence of stability and electronic structure on the specific ligands involved. Efforts to use the low oxidation state rare-earth chemistry as a guide to low oxidation state actinide chemistry will be described as well as the development of new classes of actinide complexes with low oxidation states.

NUCL 43

Review of synthesis, spectroscopy, and structural characterization of the intrinsic Pu(IV) colloidal polymer

David L. Clark[1]*, dlclark@lanl.gov, David E. Hobart*[2,3]*. (1) National Security Education Center, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Chemistry, Florida State University, Tallahassee, Florida, United States*

Hydrolysis, polymerization, and redox reactions of Pu(IV) in acidic aqueous solutions take place simultaneously, and it has been very difficult to investigate one reaction without interference from the others. Pu(IV) hydrolyzes even in pH 1 solutions and the polymerization reactions result in an intrinsic Pu(IV) colloidal sol that can disaggregate, remain suspended in solution, form gels and precipitates, or age into relatively insoluble materials, depending on the solution conditions. We have carefully reviewed and summarized 60 years of experimental data on the synthesis, spectroscopy and structural characterizations of the intrinsic Pu(IV) colloidal polymer in the 2nd Edition of the Plutonium Handbook. In this presentation, we give an overview of the spectroscopic and structural data analyzed in that review.



Electronic absorption spectrum of purified Pu(IV) colloidal sol in 0.01 M HCl (black) compared to that of Pu(IV) aquo ion in 1 M $HClO_4$ (red), replotted from original data of the authors.

NUCL 44

Exploring the actinide series from periodic trends to electronic structure and bonding

Samantha K. Schrell[2], *sschrell@lanl.gov, Jing Su*[2]*, Shane Galley*[1]*, Thomas E. Albrecht-Schmitt*[3]*, Enrique R. Batista*[4]*, Maryline Ferrier*[2]*, Stosh A. Kozimor*[5]*, Veronika Mocko*[2]*, Brian Scott*[2]*, Cayla Van Alstine*[1]*, Frankie D. White*[3]*, Ping Yang*[4]*. (1) Chemistry, Florida State University, Tallahassee, Florida, United States (2) Los Alamos National Lab, Los Alamos, New Mexico, United States (3) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (4) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (5) Los Alamos Natl Lab, Los Alamos, New Mexico, United States*

Transplutonium elements are typically generalized as being lanthanide like due to the stability of the 3+ oxidation state and their core-like *f*-electrons. In fact, the 4*f* and 5*f* elements do have a lot of similar chemical and physical properties, which has led to problems both environmentally and in advance nuclear fuel cycles. It has been suggested that soft donor (S and N) ligands might have a more covalent interaction with actinides over lanthanides due to better spacial and energy overlap of their orbitals.

Unfortunately closing this knowledge gap is difficult because of the limited supply of mid-late actinides and their high levels of radioactivity. Recently there has been a renaissance in transplutonium synthesis that has helped us gain a better understanding of these elements. Here we set out to better understand the interactions of transplutonium elements with S and N donor ligands. To do this we prepared $An(S_2CNEt_2)_3(N_2C_{12}H_8)$ (An^{III} = Am, Cm, and Cf) and compare their structure, spectroscopy, and electronic structure calculations. These results include the first Cm–S and Cf–S bond measured from a molecular crystal structure with and average bond length of 2.862 ± 0.04 and 2.836 ± 0.04 Å respectfully.

NUCL 45

From Glenn T. Seaborg via the transuranium elements to Thomas E. Albrecht-Schmitt

Thomas Schleid, *schleid@iac.uni-stuttgart.de. Institute for Inorganic Chemistry, University of Stuttgart, Stuttgart, Germany*

Back in the 1940s Glenn T. Seaborg and his transuranium team in Berkeley (CA) started to extend the periodic table of the elements by neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium and lawrencium. Before they reached the so-called fermium barrier this was possible by bombarding suitable uranium or transuranium isotopes with neutrons. Beginning with fermium, however, no elements with atomic numbers larger than 100 and masses heavier than 257 can be synthesized this way. So mendelevium, nobelium and lawrencium needed to be obtained by fusion of transuranium targets with atomic particles such as helium, boron or carbon in order to complete the actinoid series. For the discovery of most transactinoid elements even heavier species like oxygen (Berkeley, USA), neon and chromium (Dubna, Russia), iron (Darmstadt, Germany) or zinc (Wako, Japan) were accelerated to hit either transuranium or lead targets. Obtained and isolated by one of these sophisticated methods, element 106 was named after Seaborg (1912 − 1999) himself, while he was still alive. With more than a million years of half-life, several isotopes of plutonium, neptunium and curium allow even a rather lazy preparative chemistry to synthesize and characterize their plethora of compounds. For americium, the longest half-life isotope lasts for almost 7500 years only and this time shortens for berkelium to 1400 years and for californium to 2700 years. Thomas E. Albrecht-Schmitt and his team in Tallahassee (FL) brilliantly perform their difficult hydrothermal and solid-state chemistry, especially with his favorite oxoanions borate, phosphate, selenate and iodate like no one before to bask in the glow. Half-lifes of little more than 1 year and just 100 days for einsteinium and fermium, respectively, seem to hamper the chemistry of these super-heavy "post-californians" drastically and most probably make einsteinium the final frontier for chemistry on the edge of stability.

NUCL 46

Exploring *in-situ* hydrothermal redox chemistry with the *f*-elements

Eric M. Villa, *EricVilla@creighton.edu. Chemistry Department, Creighton University, Omaha, Nebraska, United States*

The investigation of hydrothermal oxidation–reduction reactions has yielding many interesting structures with a variety of applications. These redox reactions often proceed *via* convoluted mechanisms. The reactions studied here involve the use of a redox active actinide cation with a redox active ligand. Here we will explore the *in-situ* hydrothermal redox chemistry of the *f*-elements through the single crystalline products obtained; when followed carefully, these products help to yield valuable insights into these unique processes. Furthermore, we will show how this work out of the Albrecht-Schmitt lab has developed into undergraduate research projects focusing on the formation of new lanthanide compounds *via* hydrothermal *in-situ* ligand redox reactions.

NUCL 47

Chelation strategies and applications for large s-, p-, and f-block metal ions

***Justin J. Wilson**, jjw275@cornell.edu, Nikki A. Thiele, Aohan Hu. Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States*

Although ligand field stabilization dominates the coordination chemistry of the transition metals, these effects are absent for other metal ions that do not use valence d orbitals for bonding, such as the alkali, alkaline earth, and lanthanide ions. The bonding interactions of these latter ions are instead dictated by electrostatic interactions, the strength of which scales inversely with ionic radii. As such, large s-, p-, and f-block ions form coordination complexes of low thermodynamic and kinetic stability compared to their smaller counterparts. In this presentation, we discuss our efforts to develop chelating agents that can stabilize these large ions. Furthermore, we describe our use of these chelating agents for various applications in imaging, nuclear medicine, and industrial processes. This presentation underlines both the fundamental coordination chemistry principles and practical application considerations for this class of ions.

NUCL 48

Actinide endohedral fullerenes: Molecular structures and unique bindings

***Ning Chen**, chenning@suda.edu.cn. Soochow Univeristy, Suzhou , China*

The hollow internal cavity of fullerene buckyballs, e.g. C_{2n}, has been known to able to encapsulate novel metallic units, especially those otherwise very reactive or virtually impossible to prepare clusters. In this talk, *w*e will present our recent studies of a novel family of fullerenes, actinide endohedral fullerenes. The synthesis of Th@C_{82}, U@C_{2n}, ($2n$ = 72, 84) and their unique electronic properties will be discussed. Moreover, we reveal the discovery of a long sought-after unsupported U=C in an unpredicted UCU@I_h-C_{80} compound. This study suggests that actinide endohedral fullerenes not only demonstrate substantially different bond motif and cage structures from those lanthanide fullerenes and also reveal unique actinide bonds which have never been discovered in the conventional actinide compound reported previously.

NUCL 49

Synthesis of rare-earth chalcogenide nanomaterials

***Sarah L. Stoll**, sls55@georgetown.edu, Rida Atif, Dane Asuigui, Priscilla Glaser. Georgetown University, Washington, District of Columbia, United States*

We are interested in developing new synthetic methods for phase control of LnX, LnX_2 and Ln_3X_4 phases of lanthanide (Ln) chalcogenides (X = S, Se, Te). The solution phase synthesis of lanthanide chalcogenide nanomaterials has been challenged by the oxophilicity of the lanthanides, and limited range of potential precursors. Another factor is the large differences in solution redox couple between LnIII/LnII and the difficulty in stabilizing soluble divalent precursors, where the divalent state is important in the solid state for phases such as $Ln^{2+}X$, and $Ln^{2+}(Ln^{3+})_2X_4$ for Ln = redox active lanthanide. This talk will highlight recent results in the use of divalent and trivalent precursors, and the implications for nucleation and crystallization of novel rare earth nanomaterials.

NUCL 50

Design and synthesis of 3,2-HOPO-grafted chitosan oligosaccharide nanoparticles for the removal of uranium and reactive oxygen species (ROS) *in vivo*

***Juan Diwu**, diwujuan@suda.edu.cn. Soochow University, Suzhou, Jiangsu, China*

Due to the uranium mining and the potential occurance of nuclear accidents and nuclear terrorism events, the highly toxic actinides, especially uranium could be introduced into body through ingestion, inhalation, and wound related absorption. Uranium, which poses high radio- and chemo-toxicities, is mainly deposited in kidneys and bones as the stable hexavalent uranyl ion (UO_2^{2+}). Animal assays have demonstrated that chronic internal exposure to uranium can lead to renal damage and even renal failure, while long-term irradiation of femurs can consequently result in a risk of osteosarcoma. In addition, UO_2^{2+} can stimulate cells to generate reactive oxygen species (ROS), giving rise to mitochondrial and lysosomal membrane damage. At present, chelation therapy is considered to be the most effective method to accelerate the excretion of actinides from body. However, the strategy of simultaneous removal of actinides and their induced-ROS *in vivo* has seldom been considered. We therefore designed and synthesized 3,2-hydroxypyridinone-modified chitosan oligosaccharide nanoparticles (COS-HOPO,) aiming at simultaneous removal of uranium and the induced-ROS *in vivo*. Current data suggest that the combined advantages of COS and HOPO endow the new COS-HOPO nanomaterial with low toxicity, high decorporation efficiency, and good radiation protection effects.

NUCL 51

Fundamental differences of the lanthanides and later actinides in non-aqueous conditions

***Frankie D. White**, white.deuce@gmail.com, Matthew Marsh, Cristian A. Celis-Barros, Alyssa Gaiser, David Dan, Thomas E. Albrecht-Schmitt. Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

The later actinides (Am-Cf) have been significantly underexplored in comparison to the early actinides because of their similarities to the lanthanides. This area of research has recently gained interest because of the need to separate americium and curium from lanthanides in spent nuclear fuel. In lanthanides and later actinides, coordination and redox chemistry dominate. Albeit the later actinides core *f*-orbitals are much shielded like the lanthanides, the slight difference in this shielding allows for small differences to be observed. By utilizing non-aqueous conditions, the extents of these differences can be expanded from pure aqueous media. Herein, the cooridination and redox differences between the lanthanides and later actinides are observed through solid state, electrochemical, and computational analyses in non-aqueous and air-free environments.

NUCL 52

Preparation of Tc-doped TiO_2 by simple aqueous chemistry and leaching leaching behavior of Tc

***Wayne W. Lukens**, wwlukens@lbl.gov. MS 70a 1150, Lawrence Berkeley Natl Lab, Berkeley, California, United States*

Technetium (^{99}Tc) is among the most problematic fission products in nuclear waste due to its high fission yield (6%), long half life (0.21 Ma), and the environmental mobility of pertechnetate, TcO_4^-, the most stable form of technetium in aerobic environments. Technetium can also create problems during processing of spent nuclear fuel and during vitrification of nuclear waste. In particular, Tc(VII) species can evaporate from the glass melt unless the electrochemical potential is sufficiently reducing. Alternatives to glass include waste forms based on environmentally stable natural analogs such as Synroc (titanate ceramic) or TiO_2 itself. The incorporation of Tc into TiO_2 nanoparticles means of simple, aqueous chemistry is presented starting from TcO_4^- in 5 M nitric acid. A combination of X-ray diffraction, X-ray absorption fine structure spectroscopy, and UV-Visible spectroscopy reveals that pairs of Tc(IV) ions replace pairs of Ti(IV) ions in TiO_2. Tc-doped TiO_2 samples were suspended in deionized water under aerobic conditions, and the release rate of Tc under these conditions was determined. The results of this work show that Tc leaches too quickly from the TiO_2 nanoparticles for them to be viable waste forms. Comparison with the leach rates of Tc-doped iron oxides strongly suggests that the leach rate of Tc from iron oxide and TiO_2 nanoparticles is controlled by solid state diffusion.

NUCL 53

5f-Electron behavior of actinide nanoparticles embedded in porous frameworks

Stefan G. Minasian[1]*, sgminasian@lbl.gov, Augustin Braun*[1]*, Selim Alayoglu*[2]*, Corwin Booth*[3]*, Alexandre Herve*[4,1]*, Yangdongling Liu*[1]*, Trevor D. Lohrey*[5]*, Liane M. Moreau*[6]*, Daniel Olive*[7]*, Mark Straub*[5,1]*. (1) Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California, United States (2) Chemical Sciences, Lawrence Berkeley Laboratory, Berkeley, California, United States (3) LBNL, Berkeley, California, United States (4) Laboratoire Chimie de la Matière Condensée de Paris, Sorbonne University, Villejuif, France (5) University of California, Berkeley, Berkeley, California, United States (6) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States (7) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Improving the economics of nuclear power in the United States will require advanced nuclear fuels that can achieve longer service lifetimes and enhance safety margins. Recent research has shown that fuels can be designed with nanometer-sized grains to increase radiation tolerance and impart fission gas retention and heat transfer capabilities. Further improvements in the performance of advanced nuclear fuels will require an ability to control the size and composition of actinide nanomaterials, and to understand the advantages and potential limitations of exploiting nanoscale chemistry in fuel designs. Harnessing this complex nanoscale chemistry will require access to a region of actinide synthetic space that is relatively unexplored and beyond current predictive capabilities.

The primary objective of this work is to establish new methods to synthesize actinide nanoparticles (NPs) in a manner that provides control over size and composition. Our efforts to synthesize actinide nanoparticles began by conducting mechanistic studies of chemical and thermal decomposition using porous organic frameworks as inert templates. A comprehensive imaging and spectroscopic effort showed that the templates limited nanoparticle growth to 1-3 nm, which is similar to the pore size (3 nm). Nanoparticle composition was varied to include actinide dioxide or tetrafluoride (AnO_2 or AnF_4) phases by varying the precursor chemistry and decomposition conditions. Because the synthetic targets are complex, multi-component systems with hierarchical structure, a multi-pronged imaging and spectroscopic characterization strategy has been developed to ensure that definitive analyses are conducted on well-defined materials. For example, small-angle X-ray scattering, transmission electron microscopy, and ptychography are used to probe nanocrystal size, while oxygen K-edge and actinide L_3-edge X-ray spectroscopies are used to determine composition. This presentation will discuss our synthetic and characterization efforts, as well as recent progress in evaluating 5f-electron behavior with changes in size and composition at the nanometer level.

NUCL 54

Binding preference determination of lanthanum and ytterbium with beta-diketones

Eva S. Auxier[1], *eauxier@vols.utk.edu, Deborah A. Penchoff*[2], *George K. Schweitzer*[1], *Howard L. Hall*[3]. *(1) University of Tennessee, Knoxville, Jefferson City, Tennessee, United States (2) , Institute for Nuclear Security, Knoxville, Tennessee, United States (3) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States*

Separation and extraction of rare earth elements, which includes the lanthanides, has been studied for decades, but has received renewed attention in recent years due to the increasing demand for these elements for a variety of industrial applications. Since liquid-liquid extractions are the most widely-used industrial process for extraction and separation of these elements, a large variety of ligand combinations, solvents, and alterations in conditions have been investigated to increase the efficiency or selectivity of extraction from mixed-lanthanide solutions.
Binding preference characteristics of lanthanum and ytterbium complexed with various beta-diketonate ligands will be discussed. Results will include structural and thermochemical properties of lanthanum- and ytterbium-complexed with acetylacetone [acac], hexafluoroacetylacetone [hfac], 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione [fod], and 2,2,6,6-tetramethyl-3,5- heptanedione [dpm], in various solvent environments.

NUCL 55

Exploring the speciation and redox chemistry of technetium-99 using polyoxometalates as highly controlled metal oxide mimics

Shejla Pollozi[1,2], *spollozi@gradcenter.cuny.edu, Ramsey Salcedo*[1,2], *Estefania Valencia*[2], *Donna M. McGregor*[3,1], *Gustavo Lopez*[3,1], *Lynn C. Francesconi*[4,1]. *(1) Chemistry, The Graduate Center of City University of New York, New York, New York, United States (2) Chemistry, Lehman College of City University of New York, Bronx, New York, United States (3) Chemistry, Lehman College CUNY, Bronx, New York, United States (4) Chemistry, Hunter College of CUNY, Bridgewater, New Jersey, United States*

Technetium-99 (^{99}Tc) is a long-lived fission product of ^{235}U and separating it from nuclear storage tanks, characterizing it and coming up with a long-term storage solution remains a challenge. It is therefore important to understand the speciation, coordination environment and oxidation of ^{99}Tc. Polyoxometalates (POMs) are inorganic metal oxide clusters able to simulate solid oxide materials. They are chemically robust, nontoxic and present diverse elemental compositions with varying redox and electronic properties, thus making them ideal model systems within which to study the behavior of ^{99}Tc. Since POMs can be reduced using sunlight or electrolysis and can shuttle multiple electrons without losing their structural properties they can be used to potentially reduce and complex ^{99}Tc species of high or low valency. This allows for the potential stabilization of the reduced metal in an environment that can both be well controlled and well characterized. In this presentation, we use vanadium-substituted Keggin (PW_{12}) POMs,

which present both hard and soft binding sites to explore the binding and redox properties of ^{99}Tc and its non-radioactive analog rhenium.

NUCL 56

Covalency in heavy actinide dithiophosphinates

Ryan Greer[1]*, greer.rdm@gmail.com, Thomas E. Albrecht-Schmitt*[2]*. (1) Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

The separation of actinides from lanthanides from industrial wastes remains an issue of critical importance. To better design new systems to do so, it is pertinent to thoroughly investigate the character of systems already capable of these separations. In the dithiophosphinates, a family of ligands known to select for trivalent 5f ions over 4f ions, enhanced covalency in the former has been suggested and investigated as the selection mechanism. Both the synthesis of a more complete series of actinide complexes with these ligands, as well as their analysis with less-typical characterization methods are beneficial to exploring this suggestion. Dithiophosphinate complexes of americium and beyond will be synthesized and structurally characterized with helium-temperature single-crystal X Ray Diffraction. These characterizations will be used in computational and Charge Density studies, which will be subjected to analysis via the Quantum Theory of Atoms in Molecules. The extension of the isostructural series to heavier elements will aid intra-actinide-series comparisons, and the two-pronged theoretical/semi-empirical QTAIM analysis will assist both in quantifying and comparing bond characteristics as well as confirming results.

NUCL 57

Evaluation of N-donor ligands for selective minor actinide separations

Morgan L. Brown*, mlbrown44@students.tntech.edu, Jesse D. Carrick, Cory A. Hawkins. Tennessee Technological University, Cookeville, Tennessee, United States*

Development of efficient minor actinide separations for post-plutonium/uranium redox extraction (PUREX) raffinate relies on solvent extraction selectivity between trivalent actinides and lanthanides. New modular synthetic routes to N-donor metal ion ligands for this purpose are being developed. Target tridentate 2,6-*bis*-triazinyl-pyridines and tetradentate 6,6’-bis-trazinyl-bipyridines (BTP/BTBP) ligands are being screened for their solubility and stability in process-relevant solvents, as well as Am/Eu solvent extraction selectivity. Protocols have been optimized to identify ligand candidates that could provide potential improvements compared to current BTP/BTBP ligand designs. Viable candidates move to phase 2 for synthetic scale-up and systematic analysis. Solvent extraction phase distribution equilibria are being studied across a range of conditions. Along with metal ion-ligand complexation equilibria, these studies provide a

means to assess the efficacy of these new extractants and support structural models to direct synthetic priorities. In this presentation we offer a brief review of the solvent extraction chemistry of lanthanides and actinides, highlight outcomes from the first and second phases of this project.

NUCL 58

Dissolution and stability of the bismuthate species in the presence of fission products

Jeffrey Einkauf, *jeinkauf@tamu.edu, Jonathan Burns. Center for Nuclear Security Science & Policy Initiatives, Texas A&M University, College Station, Texas, United States*

The dissolution rate and solubility of sodium bismuthate has been investigated as a function of temperature and nitric acid concentration in the presence of metal ions relevant to the used nuclear fuel recycle. Sodium bismuthate has established itself as the benchmark chemical oxidant (+2.03 V vs SHE) to produce Am(VI), as AmO_2^{2+}, in aqueous nitric acid system from 4–8 M HNO_3. While near quantitative conversion to Am(VI) has been widely observed, the reaction suffers from slow kinetics, believed to stem from the limited solubility of sodium bismuthate in these systems. A fundamental knowledge of the dissolution kinetics and the behavior of the bismuthate species in solution is lacking. Initial results suggest an increased dissolution rate with increases in both temperature and acidity, along with a salt-assisted rate increase. The stability of the bismuthate ion, on the other hand, seems to decrease with increases in both temperature and acidity. Investigations into the stability of the bismuthate ion in the presence of fission product metals in solution were also carried out. Herein, we will present an overview of the dissolution and stabilities and discuss the results in regards to used nuclear fuel recycling.

NUCL 59

Reduction of uranium hexafluoride with a room temperature ionic liquid (1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide)

Cassara J. Higgins, *higgic2@unlv.nevada.edu, Katherine I. Luebke, Kenneth R. Czerwinski, David W. Hatchett. University of Nevada - Las Vegas, Las Vegas, Nevada, United States*

The United States currently has 700,000 metric tons of depleted uranium hexafluoride (DUF_6) in cylinders. There is a need to develop methods for reducing the amount of DUF_6 and the corresponding risk of corrosion and release of the volatile substance into the atmosphere. Current methods utilize vaporized DUF_6 that reacts with steam, H_2, and N_2 gases to produce uranium oxides and HF gas that must also be captured. In the current studies solid DUF_6 at depressed temperature was introduced to the room temperature ionic liquid, 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide

([MPPi][TFSI]) by simple addition. The addition DUF_6 to the IL results in the spontaneous dissolution to form a green solution through the oxidation of TFSI and reduction of UF_6 to UF_6^{2-}. At concentrations below 1 M the solution is stable and the dissolved UF_6 remains soluble in the IL. However, above 1 M a green precipitate is formed which can then be filtered directly from the IL. This precipitate is air stable once removed from the [MPPi][TFSI]. TGA analysis indicates that 58% of the mass is lost at temperatures exceeding 1148 ^oC. PXRD shows that a bulk of the product after TGA-DSC is UO_2 after exposure to air. The TGA/DSC analysis suggests the decomposition of $[MPPi]_2[UF_6]$ to UO_2 through the loss of cation species and F. Additional studies are being conducted to evaluate pathways to uranium reduction from the decomposition of $[MPPi]_2[UF_6]$ to form metal. The electrochemical reduction of UF_6 to U metal is also targeted using the UF_6 dissolved in IL.

NUCL 60

Metal flux syntheses of actinide silicide intermetallics

Wes Potter[1], *wmpotter8@gmail.com, Thomas E. Albrecht-Schmitt*[2], *Susan E. Latturner*[3]*. (1) Florida State University, Tallahassee, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (3) Chemistry, Florida State University, Tallahassee, Florida, United States*

We are exploring metal flux synthesis in search of highly refractive, stable actinide multinary intermetallics that may exhibit interesting magnetic phenomena or be suitable for nuclear waste repositories. The reactions use an excess of a low melting metal (e.g., gallium, mp 30 °C, or aluminum, mp 660 °C) as solvents for other elements. Our reactions of UO_2 and Si in Al flux have produced cubic crystals of $U_8Al_{19}Si_6$ (z=8), a new stuffed superstructure of $U(Al,Si)_3$. Diffraction measurements (X-ray and neutron) reveal aluminum and silicon ordering, as well as Al atoms “stuffed” into specific interstices throughout the crystal structure. This compound appears to be stable to 5 M NaOH, 1 M HCl, air, and water. Attempts to synthesize a thorium analog of this new cubic structure has resulted a tetragonal supercell analogous to a previously reported tetragonal $U(Al,Si)_3$ superstructure. Attempts to make Np and Pu analogs of $U_8Al_{19}Si_6$ are underway.

NUCL 61

Oxoamide and thioamide ligands for solvent extraction applications from used nuclear fuel: Investigating actinide vs lanthanide extraction selectivity

Ingrid Lehman-Andino[1], *ingrid.lehman@gmail.com, Travis S. Grimes*[2], *Jeffrey R. McLachlan*[1], *Christopher J. Dares*[1], *Konstantinos Kavallieratos*[1]*. (1) Department of Chemistry & Biochemistry, Florida International University, Miami, Florida, United States (2) Aqueous Separations & Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States*

Trivalent actinides (An^{3+}) and lanthanides (Ln^{3+}) are present in used nuclear fuel (UNF). Their separation is needed for an effective transmutation process that can increase the capacity of geological repositories. ^{241}Am ($t_{1/2}$=433 years) is one of the long-lived minor actinide isotopes present in UNF that is responsible for a great part of its radiotoxicity and heat generation. An/Ln separation processes and minor actinide recycling can increase uranium utilization. Challenging separation problems can arise for the separation of $Ln^{3+}$from An^{3+} because of their similar properties. Ligands with soft sites can take advantage of the slight difference in hardness between An^{3+} and Ln^{3+} either as organic complexants or as aqueous holdback or stripping agents. In our previous work we have investigated the selectivity for An^{3+} vs. Ln^{3+} binding and extraction using dipicolinamide analogs containing the C=O vs. C=S groups in solution, gas-phase, and by DFT calculations. Analogous water-soluble diamides and dithioamide derivatives of dipicolinic acid are used as selective holdback reagents like TALSPEAK for separation of ^{241}Am from ^{154}Eu. We will discuss solvent extraction with HDEHP in *n*-dodecane and diamides/dithioamide ligands in aqueous media with spikes of ^{241}Am, ^{154}Eu, and ^{139}Ce. The diamide ligand, *N',N''*-bis(pyridin-2-ylmethyl)pyridine-2,6-dicarboxamide has demonstrated excellent separation at pH = 2.0 between Eu/Am (SF = 74) and Ce/Am (SF = 202). Slope analysis of log D vs. log [ligand] suggests a 1:3 metal/ligand complexation ratio, which is consistent with our prior work. Our system and its complexation properties were characterized by several analytical techniques including UV-Vis and NMR titrations, as well as electrochemistry.

NUCL 62

Effects of metal flux composition on the growth of uranium silicide intermetallics

Ashini S. Jayasinghe[1]*, ashinishamindra@gmail.com, You Lai*[2]*, Ryan E. Baumbach*[2]*, Susan E. Latturner*[1]*. (1) Chemistry, Florida State University, Tallahassee, Florida, United States (2) National High Magnetic Field Lab., Florida State University, Tallahassee, Florida, United States*

Metal flux synthesis uses an excess of one or more metals with low melting points to grow crystals of intermetallic phases. This provides an opportunity to grow kinetically stable complex materials at lower temperatures than those used in traditional solid-state synthesis. This growth method is, therefore, a very productive technique for exploratory synthesis. Due to their key role in the nuclear fuel cycle, actinides have gained the attention of researchers for many decades. In addition to their industrial importance, uranium compounds also exhibit interesting magnetic properties, and these become more intriguing if the f-electrons couple with d-electrons of transition metals. The current work focuses on using a variety of metal fluxes to synthesize stable actinide materials with unusual magnetic properties. Actinide silicides are of particular interest due to their refractory properties. In this study, Ga, Al, Ga/Al, Zn/Al, and Sn fluxes were used to synthesize uranium transition metal (Ni/Co/Fe) silicide intermetallics, with the flux choice having a strong effect on what products were formed. The obtained crystals (including $UNiSi_2$, $UNiSi_3$, $U_{1.05}Ni_4Al_8Si_{1.8}$, $U_2Ni_5Si_6$) were characterized using single crystal X-ray diffraction, SEM/EDS and magnetic susceptibility measurements. The stability of several products in different media and at high temperature was also explored.

NUCL 63

Spectroscopic studies of novel N-donor ligand metal ion complexation

Kari Lawson, *kllawson43@students.tntech.edu, Jesse D. Carrick, Cory A. Hawkins. Chemistry, Tennessee Technological University, Smithville, Tennessee, United States*

A desire for more sustainable nuclear fuel cycles has generated intense interest in transuranic/lanthanide separations for spent fuel reprocessing. After plutonium is removed using a PUREX-type process, the raffinate contains americium, curium, lanthanides, and other fission products. Americium is the main actinide contributor to residual heat and activity of long-term radioactive waste, and its removal would lead to more compact geologic repositories with shorter necessary lifespans. Considerable research has been dedicated to tridentate 2,6-bis(triazine)-pyridine (BTP) and tetradentate 6,6’-bis(triazine)-bipyridine (BTBP) N-donor ligands as the basis of Am(III)/Ln(III) solvent extraction selectivity. Modular synthetic chemistry is being developed to synthesize new ligands based on these scaffolds, as part of an effort to adjust the structural and electronic properties toward Am/Eu selectivity. A recent paper reported Am/Eu separation factors as high as 200 in distributions between nitric acid and a solvent of 3,3′-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine (MOB-BTP) in FS-13. Our current work includes investigation of the metal ion complexation chemistry of MOB-BTP and newly synthesized ligands using spectrophotometric methods.

NUCL 64

Oxygen isotopes in uranium oxides measured by NanoSIMS: Refining a technique for nuclear forensics

Isabelle Weisman[1,2], *WEISMANISABELLE@GMAIL.COM, Jennifer Matzel*[2], *Peter Weber*[2], *Michael Singleton*[2]. *(1) Pacific Northwest National Laboratory, Livermore, California, United States (2) Nuclear and Chemical Sciences, Lawrence Livermore National Laboratory, Livermore, California, United States*

Advances in secondary ion mass spectrometry (SIMS) over the last two decades have made possible precise methods for measuring the isotopic composition of individual radioactive particles for nuclear safeguards and forensic applications. However, worldwide trade in nuclear materials and technology means that the location of sampling is not necessarily the location of material production. Previous studies have demonstrated that the oxygen isotope compositions of uranium oxide fuels vary with the geographical location of the fuel production facility. These observations suggest that oxygen isotope measurements of uranium oxide particles may be used for source attribution (i.e. geolocation) of nuclear materials outside of regulatory control.

In this study, we present NanoSIMS $\delta^{18}O$ measurements of particles from two UO_2 standards, CRM125A and EC-NRM-106, and particles derived from two uranium oxide fuel pellets. The goals of this study were to use modern SIMS instrumentation to assess the effects of background and particle topography on the reproducibility and accuracy of oxygen isotope measurements and to demonstrate the ability to distinguish between particles of differing oxygen isotope compositions. The particles were dispersed onto a carbon planchet, and CRM-125A particles were also dispersed onto or pressed into two additional substrates (gold and silicon). The particle measurements were compared to measurements made directly on the polished surface of a CRM125A pellet. The reproducibility of measurements on the polished pellet surface was ~1‰ (1 standard deviation), and the reproducibility of particle measurements was ~3‰ at best. The choice of sample substrate did not significantly improve measurement reproducibility. Sample charging reduced the accuracy of measurements of particles >10 micrometers in size. Our measurements were able to discriminate between particles of three different isotopic compositions (1.2‰, -11.4‰, and -18.3‰). This work demonstrates our ability to produce accurate and reproducible $\delta^{18}O$ measurements and determine the optimal techniques for SIMS analyses on UO_2 particles.

NUCL 65

Structural and spectroscopic investigation of aged plutonium oxalate species

Jordan F. Corbey, *jordan.corbey@pnnl.gov, Sergey I. Sinkov, Lucas E. Sweet, Calvin Delegard. Nuclear Signatures, Pacific Northwest National Laboratory, Richland, Washington, United States*

Plutonium oxide can be synthesized via calcination of plutonium oxalate as a key step in the process to produce plutonium metal. Although they have been studied since the 1940s, the structural properties of plutonium oxalates are not well understood. Furthermore, the Pu center is known to radiolytically decompose its oxalate ligands leading to phase transformations over time. With this study, we have used powder X-ray diffraction and optical spectroscopies to monitor the transformations of plutonium (III) and (IV) oxalate species as they convert to a different yet familiar phase.

NUCL 66

Neural networks for removal of background matrix peaks from optical emission spectra

Jana Starks[1], *jstarks3@vols.utk.edu, Alexander Braatz*[2], *Paul Taylor*[2], *Matthew Cook*[1]. *(1) University of Tennessee, Knoxville, Tennessee, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The large amount of radiant energy released during a nuclear detonation fuses elements form the environment into a glassy solid referred to as Trinitite or melt glass.

These sorts of samples are of interest to scientists and are often collected by first responders after an event. By studying the formation of melt glass samples, the chemistry of the nucleation and particle formation can be predicted so that general features of the melt glass could be known before collection. Appropriate characterization of melt glass features before collection could assist in limiting the dose to first responders by reducing the time required to collect samples from high radiation environments.

Optical emission spectroscopy of a high temperature environment surrounding a continuous dusty plasma was used to study the molecular formation process of melt glass. Due to the nature of the system, the optical spectra were dominated by lines from elemental Ar and H used to sustain the plasma. In order to study the more interesting features obscured by “background” artificial neural networks and support vector machines were used to remove unwanted background features. A classification support vector machine (SVM) was used to classify collected spectra into two categories, “Urban” and “Desert” based on spectral features. SVM’s were able to classify spectra with around 98% accuracy. Linear discriminant methods had a lower accuracy and decision trees were avoided due to their tendency to over train. A supervised trained neural network was used to map the collected spectra of a complex matrix combined with a spike of interest to a spectra representative of only the spike. Once the network was appropriately trained, it was tested using the same matrix combined with a different spike.

NUCL 67

Role of surface hydroxyls on the radiolysis of gibbsite and boehmite nano-platelets

Zheming Wang[1]*, zheming.wang@pnl.gov, Xin Zhang*[2]*, Wenwen Cui*[2]*, Ying Chen*[2]*, Eric Walter*[2]*, Austin Winkelman*[2]*, Aashish Tuladhar*[2]*, zizwe chase*[2]*, Michel J Sassi*[2]*, Carolyn Pearce*[2]*, Hongfei Wang*[2]*, Sue B. Clark*[2]*, Kevin Rosso*[2]*. (1) Pacific Northwest Natl Lab, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States*

As the dominant mineral phases of the high-level radioactive waste (HLW) sludge at the Hanford Site in southwest Washington State, gibbsite and boehmite play a role in radiolytic hydrogen generation. This is an important issue for worker safety, and adds complexity to the processing of HLW sludges for vitrification. Limited evidence suggests that dehydrogenation of surface hydroxyls in boehmite and gibbsite occurs in radiation environments. In this work, platelet nanoparticles of gibbsite and boehmite with high aspect ratios were synthesized and subjected to ^{60}Co irradiation with dose levels of approximately 5 and 20 Mrad, respectively, the latter would correspond to about 1 year of irradiation dose in a typical Hanford tank. The resulting nanoparticles were analyzed by sum frequency generation – vibrational spectroscopy (SFG-VS), a surface-specific technique, and other methods including Raman spectroscopy, electron paramagnetic resonance (EPR), high resolution atomic force microscopy (HRAFM) and X-ray diffraction analysis (XRD) before and after irradiation. While both HRAFM and XRD showed that ^{60}Co irradiation caused no change in crystallinity and surface atomic structures for either gibbsite or boehmite, SFG-VS results clearly indicated over 80% removal of the surface hydroxyls after irradiation in both. Raman spectra of the irradiated samples revealed a decrease in the bulk hydroxyl content, suggesting dehydrogenation of the internal hydroxyls as well. EPR data confirmed formation of significant levels of hydrogen radical and radiation induced oxygen defects, such as O^- and O_3^-, and most of the radiolytic products formed within the gibbsite and boehmite structures remain long after the irradiation.

NUCL 68

Simulating uranium(VI) diffusion in sodium-montmorillonite as a function of chemical solution conditions

Ruth M. Tinnacher[1]*, Ruth.Tinnacher@csueastbay.edu, Jonathan C. Pistorino*[1]*, Christophe Tournassat*[2]*. (1) Department of Chemistry and Biochemistry, California State University East Bay, Hayward, California, United States (2) BRGM Epi/Des, Orleans, France*

Most nuclear waste disposal options include compacted bentonite, predominately consisting of montmorillonite clay, as part of a barrier system to minimize contaminant mobility. Uranium (U) is the primary element in spent nuclear fuel, and a potential contaminant of water resources. Uranium sorption onto clay and its slow diffusive transport away from waste canisters are expected to limit U(VI) mobility in these systems. However, their prediction is complicated by the complex mineralogical structure of montmorillonite clay, leading to two types of surface sites and clay porosities, and by the dependence of U(VI) solution speciation on chemical conditions. For instance, depending on pH and ionic strength, U(VI) may sorb onto montmorillonite due to weak ion exchange reactions or the formation of stable surface complexes. Furthermore, at the high degrees of clay compaction expected in future barrier systems, the ability of U(VI) species to access small, highly negatively charged interlayer spaces may ultimately control diffusive fluxes.

In this modeling study, we investigate how the charge of U(VI) solution species affects U(VI) sorption and diffusion behavior. For this purpose, we simplified complex *chemical* solution speciation diagrams to *charge* speciation diagrams. Furthermore, we coupled an existing U(VI) sorption model (in PHREEQC) with U(VI) diffusion calculations (in GLE) to simulate U(VI) mobility in lab-scale through-diffusion experiments over various chemical conditions. Our results suggest that there are two important parameters that govern U(VI) diffusion in these systems. Uranium(VI) surface complexation on clay edge surfaces leads to contaminant retardation, while the access of U(VI) solution species to diffuse layers in clay interlayer spaces controls diffusive fluxes. Hence on the field scale, these parameters will determine how early a plume may cross site boundaries and pose risks to drinking water resources, and the levels of U(VI) concentrations to be expected in contaminated waters.

NUCL 69

Rare-earth element interactions with uranium oxides

***Rebecca Carter**, Rcarter6@nd.edu, Amy E. Hixon. Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Geochemical conditions present during the formation and post-formation of uranium ores results in rare earth element signatures (REE) unique to each deposit. Nuclear forensics harnesses the information provided through these REE signatures to ascertain deposit types and location to identify the origin of unknown uranium materials. The REE signatures persist though uranium processing in the beginnings of the fuel cycle, however aging processes during storage can cause these materials to undergo morphological, structural, chemical, and redox changes. This study investigates the influence of REE on uranium oxide aging in an aqueous environment. Inductively coupled plasma mass spectrometry, powder X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy (SEM) are used to describe the behavior of REEs with uranium oxides (UO_2, U_3O_8-pitchblende, and carnotite) and characterize changes in the solid phase. Results of batch sorption experiments carried out as a function of pH (3-9), ionic strength (< 0.5 M $NaNO_3$), and total REE concentration (1000 ppb – 200 ppm) indicate complete sorption of REEs between pH 6-7. Sorption decreases when the ionic strength is raised, which is indicative of the formation of outer-sphere sorption complexes. An overall trend of preferential sorption of light REEs was observed regardless of solution conditions, suggesting that uranium oxide aging in REE solutions alters the solid-phase REE signature. SEM imaging did not reveal any major morphological changes.

NUCL 70

Dissolution studies of technetium sulfide under oxidizing and reducing conditions: Effect of pH and ionic strength

*Jordan Stanberry[1], Adriana Anda[2], Ravi K. Gudavalli[2], Nikolla P. Qafoku[3], **Vasileios Anagnostopoulos**[1], Vasileios.Anagnostopoulos@ucf.edu. (1) Chemistry, University of Central Florida, Orlando, Florida, United States (2) Applied Research Center, Miami, Florida, United States (3) Subsurface Science and Technology Group, MS P7-58, PNNL 331 Bldg, Richland, Washington, United States*

Past activities related to the chemical separations for plutonium extraction at the Hanford Site (WA) resulted in the production of hazardous liquid and radioactive wastes stored in underground storage tanks. Leaks of waste liquids containing a variety of contaminants from some of these tanks have caused subsurface contamination. Tc, a major contaminant of concern at the Hanford Site, is present as highly soluble TcO_4^- under the predominant oxidizing conditions at the Hanford subsurface. TcO_4^- is mobile in the vadose zone and in situ vadose zone remediation approaches are being considered to immobilize Tc and decrease its mobility to the groundwater. A combined NH_3-H_2S treatment has been proposed for the immobilization of U and Tc in the vadose zone: H_2S reduces mobile Tc(VII) to immobile Tc(IV) sulfide phases; the NH_3 treatment

increases the aqueous phase pH promoting mineral dissolution and subsequent neo-phase formation as pH decreases back to natural values after NH_3 gas treatment. The newly formed secondary minerals have the potential of covering Tc(IV) sulfide phases, physically protecting Tc(IV) from re-oxidation and mobilization.

The objective of the current work is to investigate the stability of Tc sulfide phases under conditions similar to those at the Hanford subsurface.

Batch Tc_2S_7 dissolution experiments under oxidizing conditions revealed an increase in ^{99}Tc release rate in the aqueous phase with pH increase, whereas under reducing conditions, ^{99}Tc release was negligible as expected. Furthermore, an increase in electrolyte concentration caused an increase in dissolution, but at the same time the nature of ligand (perchlorate or bicarbonate) did not seem to affect Tc-99 release in the aqueous phase. Sulfates were detected in the aqueous phase in the presence of perchlorates, whereas in the presence of bicarbonates sulfates and thiosulfates were determined.Current, experiments involve Tc_2S_7 dissolution under oxidizing conditions using synthetic groundwater saturated in bicarbonates.

Preliminary solid phase post-dissolution measurements performed with X-Ray Fluorescence revealed the presence of ^{99}Tc only in the solid phase, whereas no sulfur was detected suggesting possible conversion of the solid from a Tc-S phase to a Tc-O phase upon exposure to oxidizing conditions. Further solid phase analyses using SEM/FIB, TEM/SAED and EXAFS are undergoing.

NUCL 71

Nuclear forensic measurement impacts of uranium hexafluoride sampling methods

Jason M. Richards, *richardsjm@ornl.gov, Leigh R. Martin, Darrell Simmons, Lee D. Trowbridge, Glenn A. Fugate. Isotope and Fuel Cycle Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Determination of age of uranium materials is an important tool in geological and nuclear forensics investigations. This is typically performed by daughter ratios techniques which work well for solid materials that act like a closed system. The physical and chemical properties of uranium hexafluoride create unique challenges when trying to employ these established techniques to determine separation dates. Solid, liquid, and gas phase sampling methods were tested to determine their limitations and explore possible applications.

NUCL 72

U-He age dating of uranium hexafluoride

Michael Singleton[1], *mjsingleton@gmail.com, William S. Cassata*[1], *Will C. Beaumont*[1], *Richard M. Cox*[2], *Darrell Simmons*[3], *Lee D. Trowbridge*[3], *Glenn A. Fugate*[3]. *(1) Lawrence Livermore National Lab, Livermore, California, United States (2) Pacific*

Northwest National Laboratory, Richland, Washington, United States (3) Oak Ridge National Laboratory, Knoxville, Tennessee, United States

The headspace gas in uranium hexafluoride cylinders contains noble gases from the atmosphere along with helium produced by radioactive decay of U and its daughters. We have developed a portable mass spectrometry system for analyzing the noble gas composition of UF_6 cylinder headspace gas, with the aim of constraining a cylinder's fill and operation history. After a cylinder is filled with UF_6, the accumulation of ^{4}He from alpha decay of uranium proceeds at a rate that is determined by the mass and isotopic composition of uranium and any other alpha-producers that are present.

To test this approach, U-He age dates were measured on a variety of UF_6 sample cylinder sizes (containing 10 g to 2 kg UF_6) with enrichments ranging from 3 to 90 atom % 235-U. Cylinder headspace is sampled and purified using chemical and cryogenic trapping. The remaining headspace is then analyzed using an online variable-inlet noble gas mass spectrometer (VIMS). Samples are also collected and analyzed offline using conventional noble gas mass spectrometry. The measured U-He ages correspond well with the known fill ages and access history for UF_6 in test cylinders with fill dates that ranged from six months to 47 years.

NUCL 73

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

Michael Klosterman[1], *michael.klosterman@utah.edu, Luther W. McDonald*[2]*. (1) Environmental Engineering, University of Utah, Salt Lake City, Utah, United States (2) The Univ 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 δ^{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 to interrogate changes in the ^{18}O/^{16}O ratio along each step of two commonly employed synthetic routes. Uranyl peroxide and ammonium diuranate starting materials were first precipitated from aqueous solutions of known ^{18}O/^{16}O ratio, followed by calcination to both uranium trioxide and triuranium octoxide. Each of these calcined species was further reduced to uranium dioxide under a hydrogen atmosphere. Identification of each uranium species was confirmed using powder X-ray diffraction (pXRD), while oxygen isotope ratios of the starting materials and their corresponding products were measured using a High Vacuum Fluorination System (HVFS) coupled with Isotope Ratio Mass Spectrometry (IRMS). Results of oxygen isotope fractionation induced during processing will be discussed, along with their implications for future nuclear forensic investigations.

NUCL 74

Characterizing uranium isotopic heterogeneity in nuclear fuel pellets using nanoscale secondary ion mass spectrometry

***Ruth Kips**, kips1@llnl.gov, Peter Weber, Erick Ramon, Ben Jacobsen, Michael Kristo. Lawrence Livermore National Laboratory, Livermore, California, United States*

Secondary ion mass spectrometry (SIMS) is used for an increasing number of applications in the area of nuclear forensic science. Its high spatial resolution at high transmission and large dynamic range, as well as the relatively straightforward sample preparation process, make SIMS the technique of choice for the measurement of isotopic and trace element abundances in inhomogeneous or particulate samples. The NanoSIMS data presented in this study showed that the microscale characterization of nuclear fuel pellets by NanoSIMS can reveal potential production process signatures that may not have been detected using the typical set of bulk/macroscopic techniques applied to these types of materials. The materials analyzed include fuel fragments obtained as part of the Collaborative Materials Exercise (CMX-4) organized by the Nuclear Forensics International Technical Working Group (ITWG), as well as a fuel pellet fragment from a commercial power reactor. While the commercial fuel pellet showed a homogeneous $^{235}U/^{238}U$ ratio (within the error of analyses) across the sample, NanoSIMS imaging of the CMX-4 fuel pellet fragments showed distinct microscale variations in the uranium isotopic composition. Analysis of the ^{236}U in one of the CMX-4 samples suggested the presence of at least three uranium oxide powders of different isotopic composition ('source terms') used in the production of the pellets. Our study highlights the importance of characterizing samples on the microscale for heterogeneities that would have otherwise been overlooked and demonstrates its potential use in guiding further nuclear forensic analysis.

NUCL 75

Variation of oxygen isotopes in uranium oxide fuel pellets

*Michael Singleton, **Jennifer Matzel**, matzel2@llnl.gov, Erik Oerter, Amanda Deinhart, Naomi Marks, Michael Kristo. Nuclear and Chemical Sciences, Lawrence Livermore National Laboratory , Livermore, California, United States*

Global variation of oxygen isotope compositions in rain and snow has been well documented. A similar spatial pattern of variation is also likely reflected in the oxygen isotope compositions of waters used in the production of nuclear materials. An oxygen isotope signature may be imparted to uranium oxide materials via exchange with water or an aqueous solvent during reprocessing and/or conversion to uranium oxide. Understanding the relationship between locally derived process waters and uranium oxide materials should allow the use of oxygen isotope abundances as a signature of the provenance (production/ reprocessing site) of samples of unknown origin. We have analyzed the oxygen isotope compositions of 23 fuel pellets from 5 localities using high

vacuum fluorination and isotope ratio mass spectrometry to examine the variation in oxygen isotope compositions of UO_2 fuel pellets. We also created particle dispersions from powders of two of the fuel pellets and measured the oxygen isotope compositions of individual UO_2 particles by secondary ion mass spectrometry (SIMS). We find that UO_2 oxygen isotope compositions vary with pellet location and local water isotope compositions, with $\delta^{18}O-UO_2$ values being 5 ± 2 per mil lower than local waters on average. The standard deviation of $\delta^{18}O-UO_2$ values for different fuel pellet production lots from the same plant ranges from 0.2 to 1.4 per mil and may depend on the variability of local water sources and/or production methods. Our SIMS measurements of individual particles were able to distinguish between two different fuel pellet oxygen isotope compositions (1.2 per mil vs. -18.3 per mil). Taken together, these data demonstrate that UO_2 fuel pellets produced at the same facility using the same process result in consistent oxygen isotope compositions over time and can be distinguished from other production localities both on a bulk and particle basis.

NUCL 76

Characterization of uranyl hydroxide hydrates and the formation of uranyl peroxide

Marie C. Kirkegaard[1,2], *kirkegaardmc@ornl.gov, Jennifer Niedziela*[1], *Andrew Miskowiec*[1], *Michael Ambrogio*[1], *Ashley Shields*[1], *Brian Anderson*[1,2]. *(1) Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) University of Tennessee, Knoxville, Tennessee, United States*

We recently demonstrated evidence of a novel non-radiolytic, non-photochemical formation mechanism for solid-state uranyl peroxide from hydrated uranyl fluoride. We have now clarified the temperature and humidity conditions under which this transformation of uranyl fluoride to uranyl hydroxide and then uranyl peroxide occurs. X-ray diffraction of the hydration products suggests that the observed uranyl hydroxide intermediate is structurally similar to the layered uranyl hydroxide hydrate minerals schoepite and metaschoepite, but with a significantly expanded interlayer spacing. We further characterize this uranyl hydroxide intermediate by comparison to synthetic uranyl hydroxide hydrates, presenting a structural and spectroscopic study of synthetic metaschoepite using X-ray and neutron diffraction as well as Raman spectroscopy and inelastic neutron scattering. In addition to providing insight into the uranyl hydroxide intermediate in our peroxide formation reaction, these experiments clarify the vibrational spectra of synthetic metaschoepite and inform previous inconsistencies in the literature. In-situ experiments with humidity control reveal that the interlayer spacing of synthetic metaschoepite is highly dependent on water vapor pressure, with a subset of the interlayer water molecules easily removed and reinserted. A similar reversible expansion and contraction of the interlayer spacing is observed for the uranyl hydroxide intermediate. Further elucidation of the peroxide formation mechanism will be discussed.

NUCL 77

Multiscale microscopy study of plutonium(III)-oxalate crystal growth

Tenisha Meadows[3]*, tenisha.meadows@pnnl.gov, Jennifer A. Soltis*[1]*, Edgar Buck*[2]*, Sue B. Clark*[3]*, Cyrena Parker*[2]*. (1) Pacific Northwest National Lab, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States (3) Washington State Univ, Richland, Washington, United States*

Little is known about the fundamental science governing the early stages of plutonium(III)-oxalate crystal growth and how the conditions of early crystal growth affect the morphology of the final product. Variations in precipitation conditions may dramatically affect the size and shape of the crystals produced and understanding how these variables affect the product provides fundamental insights into the behavior and properties of plutonium(III)-oxalate. Such insight provide a more in-depth understanding that could be used in environmental and transport studies, radioactive cleanup efforts, mixed oxide nuclear fuels or even nuclear forensics. This body of work uses a dynamic approach to study early crystal growth via in situ microscopy methods. We use plutonium(III)-oxalate, an important precursor to plutonium oxide nuclear fuels, to reveal unavailable data on the kinetics of the solid-phase transformation over time in different precipitation conditions. The approach of this work involves a combination of transmission electron microscopy (TEM), scanning electron microscopy (SEM), and optical microscopy to characterize the growth and morphological development of plutonium(III)-oxalate particles. Experiments have shown that different particle morphologies and sizes can be achieved from oxalate precipitation dependent on several factors, including plutonium concentration and order of reagent addition.

NUCL 78

Supporting legal aspects of forensic cases involving illegal trafficking and the use of radionuclides

Kelly M. Elkins*, kellymelkins@hotmail.com, Brianna Kiesel. Chemistry Department, Towson University, Towson, Maryland, United States*

Since the discovery of spontaneous radioactivity at the turn of the twentieth century, the amount of radioactive material that the United States and other countries mine and use has increased. Radionuclides are used in medical equipment, smoke detectors, nuclear power plants, research, and in nuclear bombs for military use. Protocols ensure that this material is safely handled, stored, transported, protected, and disposed of properly. However, the United States Nuclear Regulatory Commission in its May 2018 fact sheet, “Backgrounder on Dirty Bombs. U. S. NRC: Protection People and the Environment” has recognized the potential use of radionuclides to create a radiological dispersal device (RDD), or “dirty bomb”. Courts are practiced in handling traditional forensic cases in which expert witnesses are called to testify on forensic biology and chemistry analyses, including human DNA typing, and controlled substance and explosives identification. Cases of radionuclide theft, use for poisonings, illegal trafficking and possession, and loss of nuclear weapons have emerged in recent years. In this

presentation, we will present questions for nuclear forensics cases for an expert witness technical testimony in nuclear forensic cases.

NUCL 79

Visualizing chemical and isotopic perturbations in heterogeneous nuclear material with direct, uncorrected isotope imaging

Evan Groopman[1]*, evan.groopman@nrl.navy.mil, David G. Willingham*[2]*, Alex Meshik*[3]*, Olga Pravdivtseva*[3]*. (1) Materials Science and Technology, U.S. Naval Research Laboratory, Washington, District of Columbia, United States (2) U.S. Naval Research Laboratory, Washington, District of Columbia, United States (3) Physics, Washington University in St. Louis, St. Louis, Missouri, United States*

Isotope analysis provides the fingerprint of certain nuclear, chemical, and kinetic processes affecting materials. *In situ* analysis at the micrometer-scale of heterogeneous nuclear materials (e.g., glassy fallout, irradiated and non-irradiated nuclear fuel) provides detailed differentiation between chemical phases and a fine-scale picture of formation and processing conditions. Secondary ion mass spectrometry (SIMS) is the premier technique for high-sensitivity, *in situ* surface analyses for elements across the periodic table. However, elemental and isotopic quantification by SIMS can be hampered when lacking well-characterized, matrix-matched standards, and by the presence of molecular and nuclear isobaric interferences from the matrix. The molecular background in SIMS can be 4-6 orders of magnitude more intense than trace elements of interest, which preclude analyses. To address some of these challenges, we designed and built the NAval Ultra-Trace Isotope Laboratory's Universal Spectrometer (NAUTILUS), a combination SIMS – single-stage accelerator mass spectrometer, which incorporates the spatial resolving power of SIMS and high sensitivity to electropositive elements, and which removes the molecular background, allowing for direct spot and ion imaging analyses. We applied the NAUTILUS to the study of core material from the Oklo natural nuclear reactor. Oklo samples provide an isotopically perturbed system suitable for studies of the long-term retention and migration of actinides and fission products in primary U-bearing crystals and coffinite to secondary minerals such as rare-earth hydroxy aluminous phosphate and galena. Direct isotope imaging without the intense molecular background yielded the discovery of fissionogenic Cs and Ba capture in Ru-rich secondary phases. We have also observed radial gradients in Zr abundance across ~150 µm U-oxide grains, with enrichments in ^{90,91}Zr near the grain boundaries. There is no correlation with Sr isotopes and no radial variation in ^{90}Zr/^{91}Zr, indicating that migration of the long-lived ^{90}Sr ($t_{1/2}$ = 28.8 y) parent of ^{90}Zr is not the cause. These could indicate radial solubility and/or U-oxide stoichiometry gradients in individual grains or migration of reactor-produced parent actinides, such as ^{239}Pu and ^{237}Np. Small regions interspersed in the aluminous phosphate show increased ^{90}Zr/^{91}Zr ratios, indicating the possible capture of live ^{90}Sr. These require further investigation.

NUCL 80

Morphological and elemental characterization of environmental actinide bearing fuel particles formed by non-nuclear weapons accidents

Gaiven Varshney[1]*, gaivenvarshney@gmail.com, Jason Cezeaux*[2]*, Abigail A. Bickley*[1]*, James Petrosky*[1]*. (1) Air Force Institute of Technology, Dayton, Ohio, United States (2) Air Force Research Laboratory, 711th Human performance Wing, Dayton, Ohio, United States*

In order to assess the environmental impact of radioactive particles released from non-nuclear accidents, detailed forensic analysis is required on particle characteristics (size distribution, shape, composition, etc.) that determine the way that a contaminant persists in and moves through the environment. Forensic analysis can also help in determining human health risks. In the present study, we have effectively isolated, identified and characterized >50 WGPu (weapon-grade plutonium) and U (uranium) fuel bearing particles with sizes ranging from 8-500 µm, which were explosively released into the environment from a Safety Test and have persisted in the environment for more than 5 decades. We have used several non-destructive methods in our analysis including SEM, EDS, digital autoradiography, and γ-spectrometry to fully characterize each particle. The isolated hot particles obtained from the Safety Test indicate a rich set of morphological features which can be differentiated from other non-nuclear accidents. The detailed analysis of actinide fuel bearing particles indicates correlations exist between shape, size, particle characters, and surface textures.

NUCL 81

Ensuring radiological emergency preparedness: EPA-NAREL's efforts in developing metrologically-traceable performance testing samples for environmental laboratories

James Burns*, burn.james@epa.gov, Charmaine Tutson, Zachary Chambers, Robert Stiles, Alison L. Tamasi, John Griggs. National Analytical Radiation Environmental Laboratory , Environmental Protection Agency , Montgomery, Alabama, United States*

As the only radiological laboratory in the EPA, the NELAC accredited National Analytical Radiation Environmental Laboratory (NAREL), serves as a member of the EPA’s environmental response laboratory network (ERLN) and is an active member in the DHS-lead Integrated Consortium of Laboratory Networks (ICLN). In these roles, NAREL, as a part of the ORIA, recognizes the importance of national preparedness for nuclear incidents.

In continuation of our mission, NAREL is developing the capability to produce and distribute performance testing samples for a consortium of labs capable of performing radiochemical analyses. These samples will represent various matrices and contaminants that will mimic the results of a nuclear incident, such as a nuclear power plant release, the detonation of a radiological dispersal device (RDD), or an improvised nuclear device (IND).

The status of our performance testing program will be presented.

NUCL 82

Direct, uncorrected, molecule-free analysis of actinides from glassy nuclear materials

David G. Willingham[1], *david.willingham@nrl.navy.mil, Evan Groopman*[1], *David Weisz*[2], *Kimberly Knight*[2]. *(1) U.S. Naval Research Laboratory, Washington, District of Columbia, United States (2) Lawrence Livermore National Laboratory, Livermore, California, United States*

Developing analytical methods aimed at evaluating the elemental and isotopic composition of working reference materials analogs has become increasingly more desirable for advancing our knowledge of the mechanisms of nuclear fallout formation. Secondary ion mass spectrometry (SIMS) is one such technique that has risen to the top of the pack due to its ability to measure isotopic heterogeneities in nuclear materials on the micrometer scale. However, no technique is without challenges. SIMS suffers from the presence of molecular isobaric interferences at any given mass-to-charge ratio. These interferences complicate the interpretation of SIMS measurements and ultimately reduce the accuracy and precision of the measured isotope ratios. At the U.S. Naval Research Laboratory, we have developed a possible solution to the issue of molecular isobaric interferences called the Naval Ultra-Trace Isotope Laboratory's Universal Spectrometer or NAUTILUS for short. The NAUTILUS combines a small geometry SIMS instrument, maintaining the ability to measure isotopic compositions with high accuracy and precision with micrometer spatial resolution, with a Single-stage accelerator mass spectrometer (SSAMS), adding the ability to dissociate molecular isobaric interferences within a stripper gas. In this work, we demonstrate the application of the NAUTILUS to the analysis of uranium doped silicate glasses as working reference materials analogs for nuclear fallout materials. These glasses range in uranium concentration from ~4 ppm to ~400 ppm and in uranium isotopic composition from 0.72% (natural) to 92.5% enriched in ^{235}U. We found that using the NAUTILUS, not only could we measure the major uranium isotopes (e.g. ^{235}U and ^{238}U) directly, but also we could measure the minor uranium isotopes (e.g. ^{234}U and ^{236}U) from the glasses without the need for background subtraction or interference corrections. More recently, we have obtained preliminary data on glasses composed of both uranium and plutonium. These mixed actinides glasses are particularly problematic for SIMS due to the increased complexity of measuring both the uranium major and minor isotopes as well as the plutonium major (e.g. ^{239}Pu and ^{240}Pu) and minor (e.g. ^{241}Pu and ^{242}Pu) isotopes within the same sample matrix. Early measurements demonstrate that these analyses are possible with the NAUTILUS.

NUCL 83

Development of synthetic nuclear melt glass representative of an urban, post-detonation environment for forensic analysis

Nathaniel Kaminski[1], *Nathaniel.Kaminski@usma.edu, Geoffrey Bull*[2], *Robert B. Gilbreath*[1], *Justin Alexander*[2]. *(1) Nuclear Engineering, United States Military Academy, West Point, New York, United States (2) United States Military Academy, West Point, New York, United States*

A method to produce surrogate melt glass representative of a nuclear detonation in New York City and Houston has been conducted at the University of Tennessee. Using the same planning process, beads of synthetic melt glass representative of a nuclear detonation in an urban city were produced, irradiated, and characterized. The purpose of creating a synthetic melt glass representative of an urban environment is to examine to the interference of elemental and isotopic differences between major cities that stem from infrastructure and geographical differences with the isotopic differences compared against a generic nuclear weapon fission fragment yield curve. The chemical composition for each urban debris sample is determined through averaging the chemical element composition obtained from U.S. Geological Survey data of three major cities consisting of New York City, Seattle, and Los Angeles. Samples were then produced through melting powdered oxide compounds in a furnace capable of heating material to 1450 ^{o}C. Each sample was exposed to a 1 MeV equivalent neutron spectrum with a total fluence of 5.7E15 neutrons/cm^2 using a 500kW research reactor located at Ohio State University. Finally, gamma spectroscopy of each sample was taken using a HPGe detector to assess isotopic inventory with experimental results compared to pre-melt chemical compound inventory.

NUCL 84

Synthesis of debris samples in controlled environments to understand the effects of mixing on radionuclide fractionation in fallout particles

Batikan Koroglu, *koroglu1@llnl.gov, Zurong Dai, Jonathan C. Crowhurst, David Weisz, Michael Armstrong, Harry Radousky, Joseph M. Zaug, Kimberly Knight, Timothy Rose. Lawrence Livermore National Laboratory, Livermore, California, United States*

Our present understanding of how environmental conditions affect radionuclide distributions in debris is severely limited. U.S. tests were usually conducted under ideal conditions in a limited range of environments (Nevada desert, Pacific islands). To predict debris chemistry in the aftermath of nuclear explosions in untested and/or non-ideal environments, fundamental observations are needed to determine key system sensitivities. In the current work, we use a recently developed experimental setup (plasma flow reactor) to synthesize debris samples under controlled conditions to investigate how radionuclide fractionation in debris change in response to mixing effects. We investigate relative condensation and speciation of uranium, iron, aluminum, and silicon on separate experiments as well as those of their binary mixtures with uranium. The plasma flow reactor enables us to collect debris at different locations (i.e.,

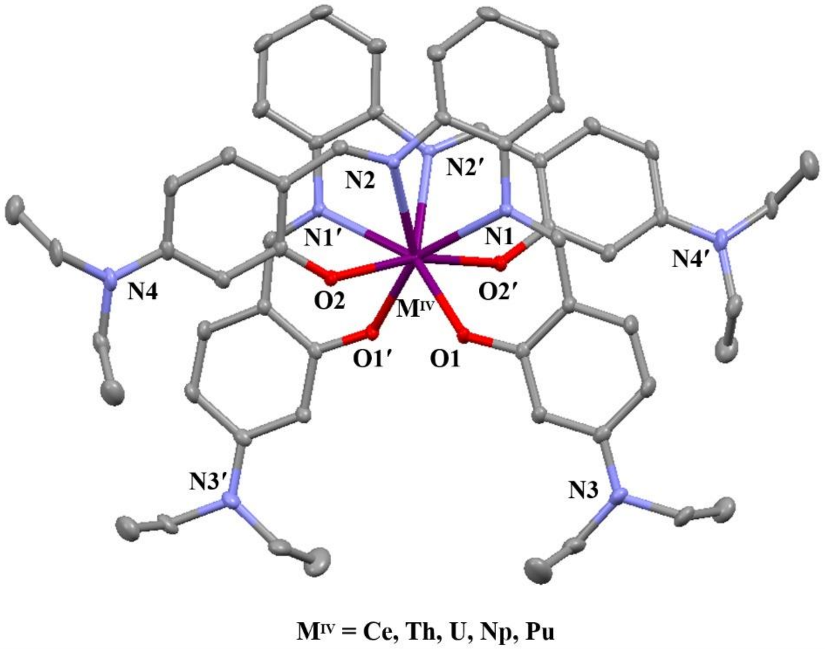
temperatures) along the system, representing different point in time during the condensation history of the reacted materials. The recovered debris samples are characterized using scanning and transmission electron microscopy to determine their size distribution and structural composition. The experimental data help gain insights into the fundamental mechanisms of homogenous vs heterogenous nucleation and relative condensation of an actinide and three major elemental constituents of environmental and structural materials.

NUCL 85

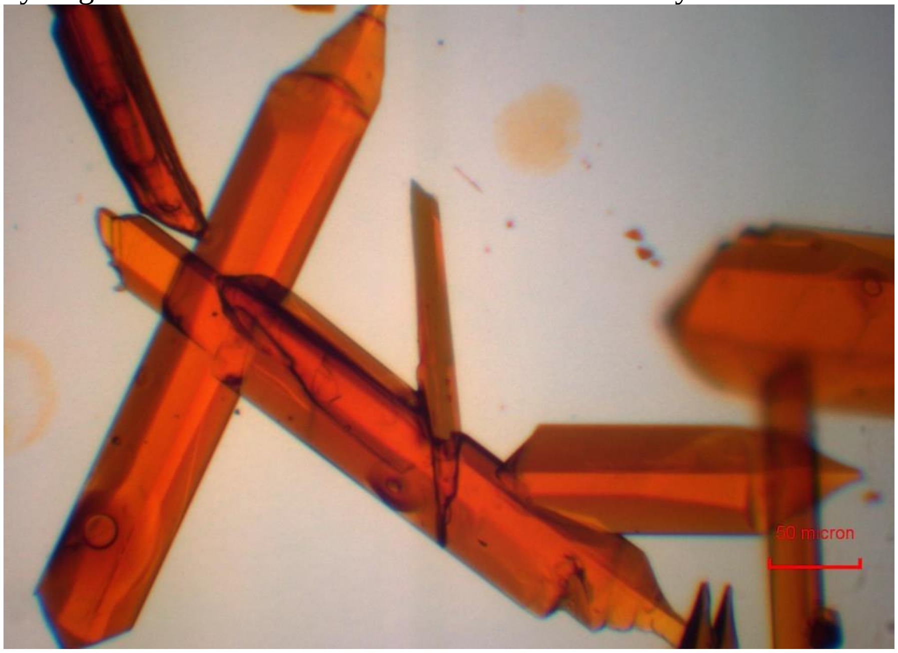
Schiff-base coordination complexes with the *f*-elements

Bonnie E. Klamm[1]*, klamm.b.e@gmail.com, Cory J. Windorff*[1]*, Cristian A. Celis-Barros*[1]*, Matthew L. Marsh*[2]*, David S. Meeker*[1]*, Thomas E. Albrecht-Schmitt*[3]*. (1) Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (2) Florida State University, Louisville, Tennessee, United States (3) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

The knowledge and understanding of fundamental actinide bonding trends and coordination modes is significantly limited compared to other elemental series in the periodic table. The lack of actinide studies limits our grasp on the bonding and electronic structure trends across the 5*f* series, and how changes in ligand binding may impact speciation and separation selectivity to different metal ions. Our interest in the chemistry of the early tetravalent actinides is based on the periodic trends through the series. Moving from Th to Pu in: ionic radius, electron configuration, ion acidity, trends in coordination chemistry and reactivity has been established. These elements and their trends provide a way to understand the structural, electronic, and chemical properties of the early actinide elements. In this study, a series of homoleptic Schiff-base complexes has been synthesized featuring a ridged phenyl backbone on a series of actinide (Th, U, Np, Pu) and lanthanide (Ce) elements. The complexes allow the comparison across a series of elements by various structural, spectroscopic, and theoretical techniques to explore the bonding differences across the metals.



Molecular structure of ML$_2$ (M = Ce, Th, U, Np, Pu; L = *N*,*N′*–bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity.



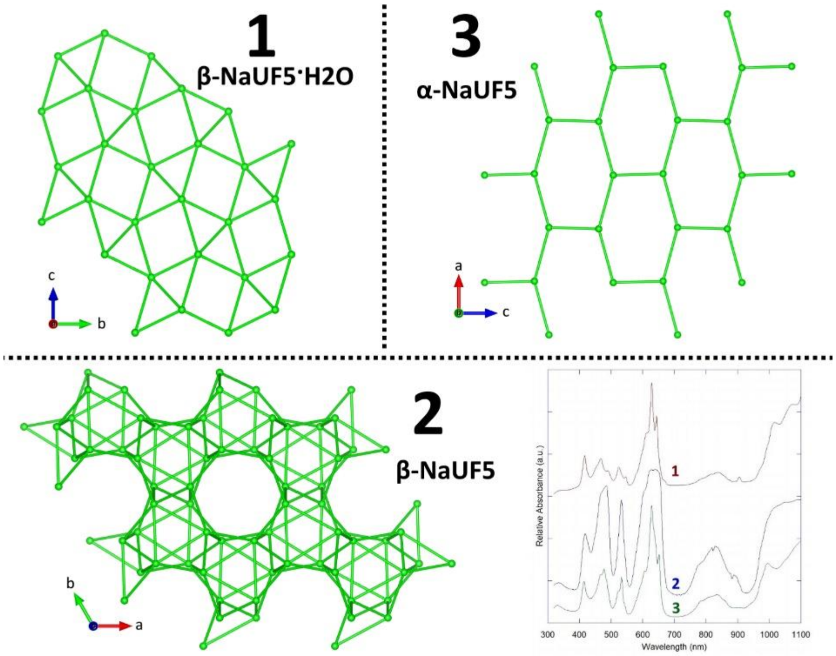
NpL$_2$ crystals.

NUCL 86

Characterization of several new ternary actinide fluorides

Alexander T. Chemey[1], *atchemey@gmail.com, Cristian A. Celis-Barros*[1]*, Kevin Huang*[2]*, Joe M. Sperling*[1]*, Cory J. Windorff*[1]*, Ryan E. Baumbach*[2,3]*, David E. Graf*[2]*, Dayán Páez-Hernández*[4]*, David E. Hobart*[1]*, Thomas E. Albrecht-Schmitt*[1]*. (1) Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (2) National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida, United States (3) Physics, Florida State University, Tallahassee, Florida, United States (4) Centro de Nanociencias Aplicadas, Universidad Andrés Bello, Santiago, Chile*

The fluorides of the early actinide series are notable for their importance in processing of materials for sensitive nuclear capabilities, as well as potential use in molten salt reactors. Much recent work has been focused on ternary and quaternary uranium fluorides, but there is necessarily an expansion of these methods to the following elements. Although there are nearly two hundred uranium fluoride structures in the ICSD, there are only eleven plutonium fluoride structures published in a similar manner, none of which is newer than 1954. Neptunium is also somewhat neglected, and there is little in the way of high-quality structural data for fluorides of this nature. Several new structures of early actinide ammonium and alkali fluorides are presented, as well as reevaluation of previously-published structures with higher quality data. A discussion of the nature of the actinide-fluoride bond is also presented, with implications for theoretical treatment of highly ionic 5*f* interactions.



NUCL 87

Explorations of high-pressure behavior of lanthanide and actinide complexes

Evan Warzecha[1]*, ewarzecha@chem.fsu.edu, Thomas E. Albrecht-Schmitt*[2]*. (1) Chemistry and Biochemistry, Florida State Universtiy, Tallahassee, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Pressure is a very effective tool for exploring fundamental chemistry. The covalency of the mid to late actinides is of ambiguous origin, and proper modeling of actinide compounds requires accurate understanding of their bonding properties. Using high pressures to tune bond distances we can tease out the origins of covalency in the actinides, which seems to have significant influences from both orbital overlap and energy degeneracy. A diamond anvil cell has been used to examine the structural and spectroscopic effects of pressure on complexes of the lanthanides and actinides. A focus will be placed on the fluorescence and absorbance spectra. The sensitivity of these spectra to pressure should increase with increasing covalent bonding character to the metal centers.

NUCL 88

Homoleptic dithiocarbamate complexes of transuranium elements

Joe M. Sperling[1]*, spjo1001@gmail.com, Thomas E. Albrecht-Schmitt*[2]*. (1) Chemistry, Florida State University, Tallahassee, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Until recently, transplutonium elements were thought to be similar to their lanthanide predecessors which have primarily ionic interactions with surrounding atoms. However, the 5f/6d orbitals of these f elements have been shown to mix with or be degenerate with the 2p or 3p orbitals of lighter atoms generating covalent interactions. Therefore, the bonding in the mid actinides tend to have some degree of covalency. There has been progress made in probing the covalency with the heavier actinides in the Albrecht-Schmitt group with the borates, dipicolinic acid, and specifically the dithiocarbamate (DTC)/ phenanthroline (phen) systems. The tris DTC/phen system is interesting due to the counterintuitive soft sulfur donors as well as their ease of synthesis. Due to pi stacking interactions present in phen, this unique system can crystalize within minutes making the compound very suitable for characterization with the high emitting actinides. This inspired the synthesis of homoleptic pyrollidinedithiocarbamate complexes to probe An-S bonding. These structures are characterized by single crystal X-ray diffraction to investigate the An-S bond.

NUCL 89

Probing plutonium redox behavior with cyclooctatetraene

***Cory J. Windorff**[1], cjwindorff@gmail.com, Joe M. Sperling[1], Bonnie E. Klamm[1], Conrad A. Goodwin[2], Daniel N. Huh[3], Alyssa Gaiser[1], David E. Hobart[1], Stosh A. Kozimor[2], Andrew Gaunt[2], William J. Evans[3], Thomas E. Albrecht-Schmitt[1]. (1) Chemistry and Biochemistry, Florida State University, Tallahasee, Florida, United States (2) LANL, Los Alamos, New Mexico, United States (3) Dept of Chemistry, University of California Irvine, Irvine, California, United States*

Despite the dearth of organometallic chemistry throughout the periodic table, organoplutonium chemistry remains rather under-developed due to the radioactivity of this element. For example, although the first organometallic plutonium compound, $Pu(C_5H_5)_3$, was first synthesized over 50 years ago, yet the structural characterization was reported just this year. To date only four organoplutonium complexes have been characterized by single crystal X-ray diffraction, all of which have been reported in the last two years. We report here the reactivity of reduced solutions of $Pu(C_5H_4SiMe_3)_3/KC_8$ with C_8H_8 leading the crystallographic characterization of the reduced plutonocene $[K(2.2.2\text{-cryptand})][Pu(C_8H_8)_2]$, and the tetrakis cyclopentadienyl ligand redistribution product, $[K(2.2.2\text{-cryptand})][Pu(C_5H_4SiMe_3)_4]$. The reaction products are similar to those obtained when $[K(2.2.2\text{-cryptand})][Ln(C_5H_4SiMe_3)_3]$ are reacted with C_8H_8, and contrast the corresponding chemistry with $[An(C_5H_3RSiMe)_3]^-$ (An = Th, U; R = H, $SiMe_3$) where only tetravalent cyclooctatetraenide products are isolated. Finally, $[Pu(C_8H_8)_2]^-$ was oxidized to $Pu(C_8H_8)_2$ and crystallographically characterized for the first time, despite being synthesized in 1970.

NUCL 90

Computational study of binding preferences across the actinide series

***Deborah A. Penchoff**[1,2], dpenchof@utk.edu, Charles C. Peterson[3], Mark S. Quint[10,11], John D. Auxier[4], George K. Schweitzer[9], Robert Harrison[5,6], Howard L. Hall[7,8]. (1) Institute for Nuclear Security, Knoxville, Tennessee, United States (2) Joint Institute for Computational Sciences, Oak Ridge, Tennessee, United States (3) Research Information Technology Services, University of North Texas, Denton, Texas, United States (4) Department of Nuclear Engineering , Institute for Nuclear Security , Jefferson City, Tennessee, United States (5) Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York, United States (6) Computational Science, Brookhaven National Laboratory, Upton, New York, United States (8) Y-12 National Security Complex, Oak Ridge, Tennessee, United States (9) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (10) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (11) US Army Nuclear and Countering Weapons of Mass Destruction Agency (USANCA), Fort Jackson, South Carolina, United States*

Computational modeling of lanthanide- and actinide-containing compounds has greatly advanced in recent years; however, deciding on methods and levels of theory of choice for these systems is often challenging as various constraints are encountered with computational cost and software limitations. Additional challenges arise from large variations in predicted properties utilizing currently available methods which can make comparisons across studies uncertain. Furthermore, experimental results which could enhance the development of computational protocols encounter constraints due to radioactivity and the need for specialized facilities.
A systematic analysis of differences observed in the prediction of structural characteristics, electron withdrawing effects, and binding energies of various actinide complexes will be presented (including nitrates, carboxylic acids, and beta-diketones). Findings discussed correspond to results obtained with density functional theory (DFT), coupled cluster with perturbative doubles and triples [CCSD(T)], complete active space second-order perturbation theory (CASPT2), and Dirac-Hartree-Fock.

NUCL 91

Functional hybrid molecules for the visualization of cancer: Dimeric BBN$_{7-14}$ dendroids combined with a bimodal molecular probe for positron emission tomography (PET) and optical imaging (OI) suited for tracking of GRPR-positive malignant tissue

Ralph Hübner, *ralph.huebner@medma.uni-heidelberg.de, Carmen Wängler. Department of Clinical Radiology and Nuclear Medicine, Medical Faculty Mannheim of Heidelberg University, Mannheim, Germany*

Bimodal imaging becomes an important growing field in medical diagnostics. Imaging and characterization of tumors can be more reliable and sustainable with a suited modality. For bimodal imaging several combinations of different physical investigation technologies are thinkable. For example PET/CT is standard in clinical practice; other combinations are under development (MRI/PET) or part of intensive investigations (OI/MRI). Here, we report dimeric peptides combined with bimodal imaging hybrid molecules suitable for OI/PET imaging. Advantage of this combination is e.g. an intraoperative image-guided surgery by fluorescent spectroscopy after a pre-imaging via PET and thus the chance of a very precise removal of malignant tissue and/or sentinel lymph nodes without radiation exposure for the surgeon by the very precise delineation of malignantly transformed tissues. Different fluorescent dyes, covering the visible to NIR window were connected to a NODAGA chelator (which binds very selectively the positron emitters ^{68}Ga or ^{64}Cu) via a short peptide sequence. In addition, we developed new fluorescent indocyanine dyes. For their design, we paid particular attention to their possible biodistribution. The different imaging building blocks were aligned to a PESIN-dimeric structure by a click reaction to form highly functional molecules. This molecular hybrid of dimeric peptide and bimodal imaging unit binds very effectively to the gastrin releasing peptide receptor (GRPR) which is for example overexpressed on human prostate carcinoma. The presentation includes synthesis, evaluation of the fluorescent-optical- and radiolabeling properties of the bimodal subunits as well as the combined dimeric bio-functional molecules. Additionally, in vitro binding studies and comparison of different other PESIN carrying structures will be presented.

NUCL 92

Application of PET neuroimaging probes targeting epigenetics

*Yulong Xu, Ping Bai, Stephanie Fiedler, Brenda Ntaganda, Yu Lan, Zude Chen, Sha Bai, **Changning Wang**, cwang15@mgh.harvard.edu. Massachusetts General Hospital, Harvard Medical School, Charlestown, Massachusetts, United States*

Molecular imaging, such as positron emission tomography (PET), has been widely used in medical research and drug discovery. We have developed new imaging tools and applied them in clinical research and drug discovery. In this presentation, I will discuss the development and application of molecular neuroimaging techniques for brain research. In the past few years, we have developed the first generation of epigenetic PET probes for HDACs and bromodomains. The first probe for class I HDAC imaging has successfully advanced to human imaging studies and shows promising results so far. With these tools, we know the epigenetic changes in patients for the first time, and we also developed a series of new epigenetic inhibitor. Our work is a unique example on the multidisciplinary research, including molecular imaging, medicinal chemistry, clinical research and drug discovery.

Figure 1

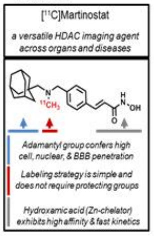


Figure 2

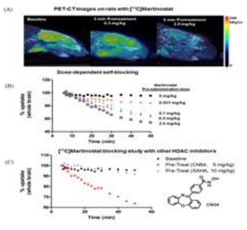


Figure 3

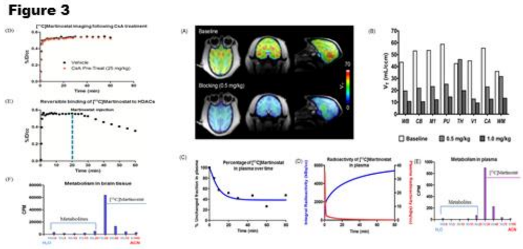
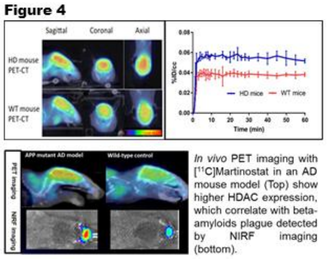


Figure 4



In vivo PET imaging with [11C]Martinostat in an AD mouse model (Top) show higher HDAC expression, which correlate with beta-amyloids plague detected by NIRF imaging (bottom).

Figure 5

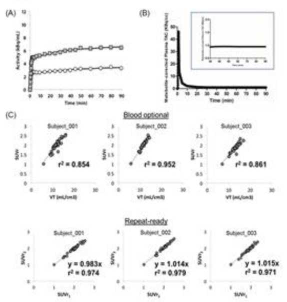


Figure 6

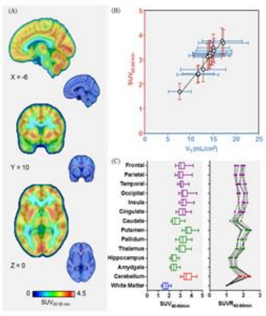


Figure 7

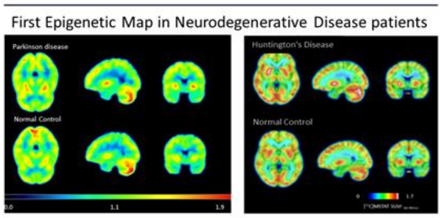
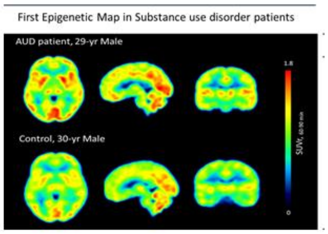


Figure 8



Please see the following Figures in the "IMAGE" file.

Figure 1. We have developed $[^{11}C]$Martinostat, incorporating three key structural features to create a versatile and translational probe for visualizing HDAC expression *in vivo*.

Figure 2. Rodent *in vivo* PET imaging with $[^{11}C]$Martinostat reveals robust and blockable uptake in brain. (A) Summed PET images (1-60 min) following injection with $[^{11}C]$ Martinostat; (B) Whole-brain tracer uptake levels, normalized to uptake at 6min, were altered by 10-40% in self-blocking experiments; (C) $[^{11}C]$Martinostat brain uptake was also blocked by 5-min pretreatment with the patent-published HDAC inhibitor CN54 (5mg/kg) but not SAHA (10mg/kg); (D) Brain uptake of $[^{11}C]$Martinostat in rats is equivalent 30 min after pretreatment with vehicle (control) or the P-glycoprotein (Pgp) inhibitor cyclosporin A (CsA, 25 mg/kg, i.v.); (E) Equilibrium binding of $[^{11}C]$Martinostat is disrupted by administration of unlabeled Martinostat (1.0 mg/kg, i.v.) 20 min after tracer injection, demonstrating reversible HDAC binding in brain.

Figure 3. Kinetic modeling results with $[^{11}C]$Martinostat in baboon brain. (A) The total volume of distribution (V_T) images from one representative animal show robust differences in radiotracer uptake at baseline and after blocking (0.5 mg/kg i.v., 10 min pretreatment); (B) Two independent baseline-blocking studies were used to resolve quantitative V_T data which show that pretreatment with unlabeled Martinostat (0.5 or 1.0 mg/kg) dose-dependently blocks tracer uptake in different baboon brain regions. WB: whole brain; CB: cerebellum; M1: primary motor cortex; PU: putamen; TH: thalamus; V1: primary visual cortex; CA: caudate; WM: white matter; (C) $[^{11}C]$Martinostat stability evaluated in baboon plasma over time showed lasting presence of 40% of parent compound at timepoints >30min. (D) Dual axis plot of baboon plasma analysis shows $[^{11}C]$Martinostat radioactivity is rapidly cleared from blood (red, right axis) while metabolite-corrected plasma integral (blue, left axis) demonstrates efficient tracer delivery to perfused tissues. (E) Radioactivity, measured in counts per minutes (CPM), was analyzed in baboon plasma 5-min post injection with $[^{11}C]$Martinostat. Minimal radioactivity was detected from polar metabolites eluted with high ratios of water to acetonitrile (ACN).

Figure 4. *In vivo* PET imaging with $[^{11}C]$Martinostat in AD, HD and WT mice. Summed PET images (1-60 min) following injection with $[^{11}C]$Martinostat. The whole brain uptake (%ID/cc) is increased in AD and HD mice, indicating that HDAC would be a promising targeting for therapeutic development.

Figure 5. (A) Metabolie-correct TAC from human plasma (30-90 min TAC in the square); (B) Time activity curves (TACs) and compartmental model fitting (two-tissue compartmental model) results for superior frontal cortex and white matter. TACs of the superior frontal cortex (square) and the white matter (circle) regions from all subjects are shown for the 90-minute scan duration. (C) (Top) High reliability in PET test-retest with $[^{11}C]$Martinostat. Excellent correlations of HDAC density measures in whole brain from same day test-retest demonstrate the stability of repeated HDAC measures. (Bottom) Quantitation of $[^{11}C]$Martinostat distribution in human brain PET scans. SUVr, standardized uptake with normalization to white matter, is purely image-based however aligns incredibly well with distribution volumes (V_T) obtained using plasma-input function from sampled arterial blood.

Figure 6. Group $[^{11}C]$Martinostat $SUV_{60\text{-}90min}$ images show small intersubject variation of localized, regional $[^{11}C]$Martinostat binding. (A) Mean images (upper left) and standard deviation images (inset on the lower right) of $SUV_{60\text{-}90min}$ from healthy volunteers (n=8). (B) Correlation of regional distribution volume (V_T) values, derived from a two-tissue compartmental model using metabolite-corrected arterial plasma as input function, and $SUV_{60\text{-}90min}$ values (n=6). The V_T values and $SUV_{60\text{-}90min}$ were significantly correlated ($r^2=0.96$; correlation analysis, $p<0.0001$). (C) *(Left)* Regional $SUV_{60\text{-}90min}$ of cortical (purple), subcortical (green), cerebellar (red), and white matter (blue) volumes of interest. *(Right)* Regional $SUV_{60\text{-}90min}$ values were normalized to the subject's white matter $SUV_{60\text{-}90min}$ value ($SUVR_{60\text{-}90min}$). Each dashed line represents $SUVR_{60\text{-}90min}$ values from a single subject (n=8).

Figure 7. We have acquired $[^{11}C]$Martinostat PET along with simultaneous MRI in a 69-year-old cognitively normal (MMSE 30) man with PD of 17 years duration, Hoehn and Yahr stage III (**Left**). HDAC density was increased in several brain regions compared to a 65-year-old normal control. Elevated HDAC density in the putamen was more pronounced on the left, correlating with the subject's greater right-sided motor impairment (UPDRS total 35; left 8, right 11). These preliminary data support the hypothesis that regional changes in HDAC expression accompany PD and relate to clinical features of disease. We have processed the data from the first HD patient (scan ID PARJ59) and this is the first PET brain image (**Right**) to show the HDAC expression in HD patients. After comparison with a control scan (female, 51 years old), we found that the uptake in right putamen and cerebellum are higher in this HD patients than this control. The images are presented as SUVr (60-90 min, normalization to the whole brain uptake).

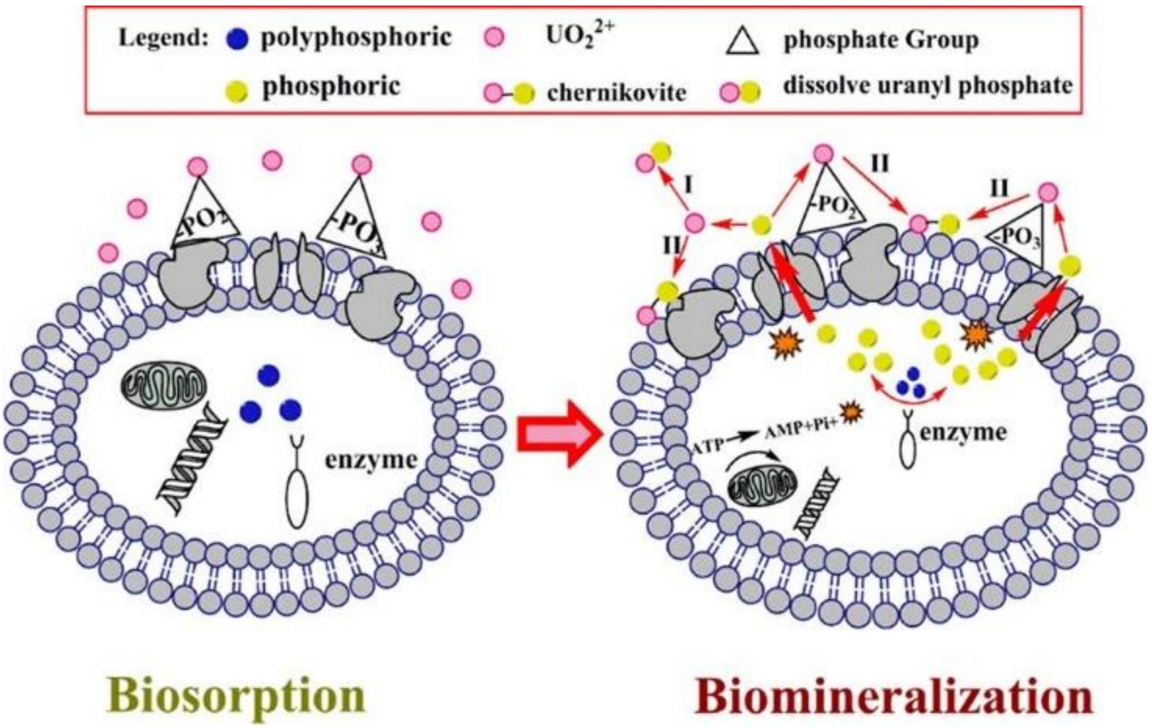
Figure 8. The HDAC PET imaging in a AUD patient (29-yr, male), compared with a control (30-yr, male). This is the direct evidence to show HDAC expression changed in SUD patient, and it is the first time to measure the HDAC expression in the living brain. The SUVr (normalized to white matter) values in brain regions indicated HDAC expression increased in this AUD patient.

NUCL 93

Synergistic biosorption and bioprecipitation strategy for *Shewanella putrefaciens* and *Kocuria* sp. to immobilizing U(VI) from aqueous solution under aerobic conditions

***xiaoqin Nie**[1,2], xiaoqin_nie@163.com, Yiqian Wang[1], Wenbo Huang[1], Congcong Ding[1], Wencai Cheng[1], Mingxue Liu[1], Faqin Dong[1]. (1) Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang, Sichuan, China (2) Argonne National Laboratory, Argonne, Illinois, United States*

In order to investigate the immobilization ways of U(VI) on Gram-positive bacteria *Kocuria* sp. and Gram-negative bacteria *Shewanella putrefaciens,* we investigated the interaction behavior under different conditions by batch experiment. U(VI) products on *Kocuria* sp and *Shewanella putrefaciens* were characterized by SEM, XRD, FTIR, and XPS techniques. SEM-EDS results presented U(VI) mineral-like precipitation formed on the cell surface which contained high percentage of P and U elements. XPS results also confirmed the appearance of bond P-O-U. XRD results showed uranium phosphate biomineral existed as chernikovite on the cell surface of *S.* p*utrefaciens.* and *Kocuria* sp. at slightly acid pH, but not at pH > 7.0. According to FTIR analysis, in addition to PO_4^{3-} groups, C=O, -OH, -COOH groups might play important roles in complexation with U(VI). The bioprecipitation process of U(VI) on *S.* p*utrefaciens.* and *Kocuria* sp. required longer time than sorption process, indicating that bioprecipitation was induced by the biosorption process. Concentrated U(VI) on the cell surface via fast biosorption might provide nucleation sites for the precipitation to insoluble minerals, while the formation of U(VI) biomineral led to the relatively permanent immobilization of U(VI). Meanwhile we found that *S.* p*utrefaciens.*cell come together before biomineralization. Our findings highlight the synergistic biosorption and bioprecipitation process of *S.* p*utrefaciens.* and *Kocuria* sp. for U(VI) immobilization, which are of significance in predicting the U(VI) immobilization properties and preventing the migration of U in aqueous. The bacterially mediated U(VI) biomineralization, more stable to oxygen over a wide pH range, will be a complementary approach to anaerobic bioreduction in aerobic environments.



NUCL 94

Exploring ionophore interaction with lanthanides and actinides

Alyssa Gaiser, *agaiser@ucla.edu, Thomas E. Albrecht-Schmitt. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Valinomycin is a naturally occurring ionophore most known for its interaction with potassium. Transporting up to 10,000 potassium ions across a cell membrane per second, valinomycin uncouples oxidative phosphorylation. For this reason, abundant research has been performed on valinomycin with alkali and alkaline earth metals; however, no research has been performed studying valinomycin with *f*-block elements until now. Identifying valinomycin's interactions with various lanthanides and actinides provides not only fundamental knowledge about these elements, but also binding affinities for potential use in medicine. Furthermore, the crystal structures of valinomycin with various lanthanides and actinides provide insight into valinomycin's structural behavior, in addition to unusual bonding behavior for both lanthanides and actinides.

NUCL 95

Investigation on complexation of uranyl with Raman spectroscopy: Coordination mode, intensity, and related Raman shift

Guoxin Tian[1,2]*, gtian@lbl.gov, Qian Liu*[1]*, Suliang Yang*[1]*, Qianci Zhang*[1]*, Dingming Li*[1]*, Yan Zhang*[1]*. (1) Radiochemistry, China Institute of Atomic Energy, Beijing, China (2) Nuclear Chemical Engineering Department, Harbin Engineering University, Harbin, China*

The change in the Raman band of uranyl, UO_2^{2+}, at about 870 cm^{-1} due to the formation of complexes with various ligands is proven to be very informative for investigating the complexation of uranyl. The linear uranyl cation unit, O=U=O, gives a strong and sharp Raman band in the range of 700-900 cm^{-1} originated from the symmetric stretch vibration (v_1) while exposed to a laser beam. The symmetric stretch vibration (v_1) of uranyl is apparently affected by the association between uranyl and the coordination ligands in the equatorial plane, and the exact change in v_1 depends on the ligands attached. By using Raman spectrometry, the complexation of uranyl ion in solutions, containing very weak/non-coordinating NO_3^- or ClO_4^- as internal standard, with weak ligands (carboxylate), with moderate ligand ($C_2O_4^{2-}$), and with very strong ligands (dipicolinic acid, DPA and fluoride) has been investigated with spectral titration method. The results suggest that the linear relationships between the concentrations of the species and the corresponding Raman band intensities can be utilized to determine their concentrations, and further to study the complexation of uranyl with various ligands.

NUCL 96

Alcohol clustering mechanisms in supercritical carbon dioxide using diffusion NMR and network analysis

Steven R. Saunders[1,2]*, steven.r.saunders@wsu.edu, Trent R. Graham*[1]*, Daniel Pope*[2]*, Yasaman Ghaadrghadr*[2]*, Aurora E. Clark*[2]*. (1) Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington, United States (2) Department of Chemistry, Washington State University, Pullman, Washington, United States*

Co-solvent clustering in complex fluids is fundamental to solution phase processes, specifically related to the use of mixed solvents and chelating agents for the extraction of lanthanides and actinides from nuclear fuel waste. The mixture of methanol in supercritical CO_2 is frequently used to enhance the extraction and recovery using phosphine-based ligands. Methanol (MeOH) clustering in supercritical carbon dioxide is explored with diffusion-based NMR (DOSY-NMR) and molecular dynamics (MD) simulations. Improved self-association models including both cooperative cluster assembly and entropic penalties for the formation of large clusters to predict the clustering will be presented. A network analysis of MD simulations show an enhanced stability of cyclic clusters, specifically tetrameric, across all MeOH concentrations and was consistent with experimental DOSY-NMR molecular cluster distributions calculated with self-association models. Simulations also reveal the emergence of cluster assembly and disassembly reactions that deviate from stepwise, monomer addition or removal. The powerful combination of experiment, simulation, and novel analyses

removes the need for contemporary approximations and enables refinement of models that describe co-solvent aggregation with far-reaching impact to the prediction of solution phase properties of complex fluids. Understanding the conditions near the alcohol cluster is critical to controlling the chemistry of extraction and will provide new engineering opportunities to improve nuclear fuel processing.

NUCL 97

Computational assistance in the supramolecular assembly of actinide hybrids

Christopher L. Cahill[1]*, cahill@gwu.edu, Robert G. Surbella*[3]*, Korey Carter*[4]*, Nicole Byrne*[2]*, Lucas Colucci Ducati*[5]*, Jochen Autschbach*[6]*. (1) George Washington Univ, Washington, District of Columbia, United States (2) The George Washington University, Richland, Washington, United States (3) Pacific Northwest National Laboratory, Richland, Washington, United States (4) Lawerence Berkeley National Lab, Berkeley, California, United States (5) Fundamental Chemistry, University of São Paulo, São Paulo, Brazil (6) SUNY Buffalo, Buffalo, New York, United States*

Our group has been synthesizing actinyl (AnO_2^{2+}An = U, Np, Pu) bearing materials using either supramolecular assembly of molecular species, or the formation of coordination polymers. Both approaches rely on non-covalent interactions (NCIs) as either the primary means of assembly, or an ancillary feature that may tune (for example) emissive properties. Crystallographic studies of materials featuring NCIs (such as H- or halogen bonds) are indeed helpful in defining regularly occurring motifs, yet often fail to indicate interaction strength, or in extreme cases, fail to indicate whether or not an interaction is even attractive. Presented will be an overview of AnO_2^{2+}bearing materials, a selection of structure-property relationships, and illustrative examples of where electrostatic surface potentials and the quantum theory of atom in molecules (QTAIM) approach have contributed to rationalizing structural motifs and ranking of NCIs.

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Revisiting the recovery of plutonium from chloride salt wastes by solvent extraction

Rebecca M. Chamberlin[1]*, rmchamberlin@lanl.gov, Diana L. Decker*[1]*, Charles H. Helma*[1]*, Donivan R. Porterfield*[1]*, Dennis P. Montoya*[1]*, Sara P. Aragon*[1]*, Ning Xu*[1]*, Kirk R. Weisbrod*[2]*, David B. Kimball*[2]*. (1) Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Operations within the plutonium facility at Los Alamos National Laboratory routinely generate residues that are too rich in plutonium to discard, but not pure enough to be used as feed for the electrorefining purification process. Chloride salt residues are currently purified for electrorefining using hydrochloric acid-based solvent extraction

process. A multi-disciplinary team at Los Alamos has been testing milli- and microfluidic contactors for use in the chemical recovery of actinides. With the possibility of enhanced mass transfer due to the high efficiency mixing in these contactors, the chemical kinetics of solvent extraction are of significant interest. The current baseline solvent system is based on tributyl phosphate (TBP) extraction, but liquid anion exchangers (Aliquat 336) have the potential to provide enhanced radiation resistance and streamline Pu recovery from spent solvents. Equilibrium and kinetic considerations for extracting plutonium from chloride salt-bearing solutions, and potential process and equipment designs, will be discussed.

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Cation exchange applications for processing plutonium-238

***Laetitia H. Delmau**, delmaulh@ornl.gov, L. F. Mora, Bradley Tinker, Dennis E. Benker, David W. DePaoli. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Although solvent extraction is a very efficient process used to separate plutonium from neptunium and fission products, it does not yield the levels of purity required for the plutonium product to be used in Radioisotope Thermoelectric Generators (RTGs) and for recycling neptunium. Ion exchange has become an indispensable method to purify neptunium and plutonium as part of the plutonium-238 production program at Oak Ridge National Laboratory. Fission products are removed by solvent extraction, follow-on separations are accomplished using ion exchange. The multiple oxidation states of neptunium have specific redox properties yielding different affinities to the anion exchange resin. Thus, very clean plutonium and neptunium products can be obtained during the elution of the column. Further purification is achieved using a cation exchange resin. The resin is used to immobilize the plutonium before calcination. This step also lets any neptunium go through the column. Plutonium obtained during the third plutonium-238 production campaign at Oak Ridge National Laboratory met all the product specifications given by Los Alamos National Laboratory. In addition, very clean neptunium containing less than 10 ppm of plutonium-238 was recently produced to make targets for test irradiations in the Advanced Test Reactor at Idaho National Laboratory.

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Real-time adjustment of Pu:U ratios in the CoDCon (modified PUREX) flowsheet

***Gabriel B. Hall**[1], Gabriel.Hall@PNNL.gov, Jarrod R. Allred[1], Amanda M. Lines[1], Sergey I. Sinkov[1], Forrest D. Heller[1], Samuel A. Bryan[2], Gregg J. Lumetta[3]. (1) Nuclear Chemistry & Engineering Group, Pacific Northwest National Laboratory, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Battelle, Richland, Washington, United States (3) MSIN P7-25, Pacific Northwest National Laboratory, Richland, Washington, United States*

The largest challenge of nuclear power production is how to safely dispose of used nuclear fuel. Processing the fuel to remove neutron poisons allows utilization of the remaining uranium and transuranic elements, including plutonium, as a mixed oxide fuel (MOX). This in turn reduces the heat load of deep geological repositories, reduces the environmental impact of uranium mining by requiring less mining, and reduces the time that the remaining used nuclear fuel is radiotoxic. The historical implementation of used fuel reprocessing in the United States has focused on the complete separation of plutonium from uranium. However, due to political changes and safety concerns, isolation of pure plutonium is no longer desirable. Bleeding a controlled amount of uranium into the plutonium product during solvent extraction will allow the direct production of MOX for commercial power production, which reduces secondary waste from blending operations, increases criticality safety, and increases safeguards security. Pacific Northwest National Laboratory is optimizing the Co-DeContamination (CoDCon) flowsheet with sixteen 2-cm centrifugal contactors, and answering several operational questions. Can the ratio of Pu:U be monitored in real-time? Can real-time adjustments be made to maintain a target ratio? What is a reasonable tolerance for the target Pu:U ratio? This presentation will present the results of the first three CoDCon tests in which we have demonstrated that online monitoring is an extremely useful tool tracking the real-time concentrations and oxidation states of the actinide elements, and real-time adjustments can be made to maintain a Pu:U ratio within 2 percent.

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What is old is new: production and purification of polonium from bismuth using TBP and TBP resin

Ali Younes[1], *aliyouness1@live.com, Cyrille Alliot*[2,3], *Anne-Cécile Bonraisin*[3], *Marcel Mokili*[4], *Ferid Haddad*[3], *Gilles Montavon*[4]. *(1) Department of Chemistry, Hunter College of the City University of New York, New York, New York, United States (2) CRCNA INSERM U892, Nantes, Saint-Herblain,, France (3) ARRONAX Cyclotron, Nantes, Saint-Herblain,, France (4) SUBATECH laboratory (UMR 6457), IN2P3-CNRS, Nantes, France*

Although the existence of polonium was considered by Mendeleyev in 1889, and its discovery made official in July 1898 by the works of Pierre and Marie Curie, the chemical properties of this element and its complexes in aqueous and biological media are still little known. This is due to its extremely low availability in the environment and the absence of stable isotopes. The annual worldwide production quantities of polonium-210 do not exceed 100 milligrams. A new method is proposed for the production and purification of polonium-210 (^{210}Po). Two approaches were investigated employing ARRONAX cyclotron. The first approach is based on the bombardment of ^{209}Bi foil with a 37 MeV alpha particle beam that produce ^{210}At which later decays into ^{210}Po. The separation of ^{210}Po from the irradiated Bi target were obtained by using solvent extraction employing tributyl phosphate as an extractant. The separation of the radiotracer of ^{210}Po (2.10^{-13} mol) from the macroscopic quantity of ^{209}Bi (3.10^{-2} mol) were performed by extraction of ^{210}Po to an organic phase (10%TBP in para-Xylene) from a

7M HCl solution and back-extracted to a 9M HNO3 phase after studying different parameters (TBP dilution degree, solvent, acid nature). The second approach is based on the irradiation of stable bismuth with a deuteron beam of 16 MeV to produce ^{210}Po, ^{209}Po and ^{208}Po. These radioisotopes were separated from bismuth by using TBP-resin. Both batch and optimized studies were performed. The achievement of this present work rely on minimizing the production time cost, increasing recovery yield and radio purity of polonium-210.

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Chemistry of the strong force

Gary L. Smith, *gsmith371@tampabay.rr.com. Retired, Winter Haven, Florida, United States*

Part 1: Propose six preon strings that afford physical structures for the electron, positron, gluons, and quarks.
Part 2: Establish more rules for coloc charge interactions (mixing), and formation of the above particles (plus).
Part 3. Propose a physical structure for the neutron (proton) that has a gluon skin surface chemistry.

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Uranium chemistry in condensing laser-induced plasmas

David Weisz[1]*, weisz3@llnl.gov, Jonathan C. Crowhurst*[1]*, Batikan Koroglu*[1]*, Harry Radousky*[1]*, Timothy Rose*[1]*, 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 chemistry of fallout-debris formation in nuclear fireball environments is controlled by multiple inter-dependent parameters, including the composition and temperature of the fireball. Understanding high-temperature chemistry is important to constraining vapor-phase fractionation, which ultimately controls condensed-phase compositions. In this work, we explore the high-temperature molecular chemistry of uranium and oxygen during plasma condensation for the purposes of constraining fallout formation conditions. To study molecular formation at relevant temperatures (<1 eV), we ablated a uranium metal target in carrier gasses having a range of oxygen concentrations to study the effect of oxygen fugacity on uranium oxide formation in the vapor phase. Ablation experiments were conducted with a pulsed Nd:YAG laser (~7 ns pulse length), and the formation of uranium monoxide (UO) was studied via time-resolved emission spectroscopy. Emission spectra were acquired (with ns-scale gate-widths and delay times) using an intensified CCD (ICCD) and a grating spectrometer. These data will be used to calibrate a computational kinetics model, which is being developed as a predictive tool for molecular formation studies in high-temperature systems by our collaborators at University of Illinois, Urbana-Champaign.

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Analysis of synthetic nuclear melt glass (urban) using x-ray fluoroscopy

Geoffrey Bull[1]*, geoffrey.bull@usma.edu, Dawn E. Riegner*[2]*, Kenji Onaka*[1]*, Nathaniel Kaminski*[1]*, Robert B. Gilbreath*[1]*. (1) United States Military Academy, West Point, New York, United States (2) US Military Academy, West Point, New York, United States*

Using a process for production of surrogate melt glass simulating a nuclear detonation previously provided through work at the University of Tennessee, a synthetic melt glass representative of material in several urban cities was produced. The purpose of creating the synthetic melt glass is to examine the challenges to nuclear forensics that elemental and isotopic differences between major cities pose. Previous work using Energy Dispersive (EDXRF) analysis indicated possible chemical composition changes of more than 10% between pre- and post-melt samples for the major elemental components. This work focuses on resolving the pre- and post-melt differences and then adding trace quantities of rare earth elements to determine the practicality of XRF for chemical analysis of surrogate materials. Samples were produced through melting powdered oxide compounds in a furnace at 1450 ^{o}C. Pre- and post-melt samples were analyzed using EDXRF. Additional samples containing higher compositions of rare earth elements were also analyzed. The resulting chemical analysis comparing post-melt samples to the initial sample compositions will be shown.